(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) **World Intellectual Property Organization**
International Bureau

(43) **International Publication Date**
24 October 2013 (24.10.2013)

WIPO | PCT

(10) **International Publication Number**
WO 2013/157660 A1

(51) **International Patent Classification**:
H01M 10/054 (2010.01) ***H01M 10/052*** (2010.01)
H01M 4/139 (2010.01) ***H01M 10/0525*** (2010.01)
H01M 4/1397 (2010.01) ***H01M 10/0565*** (2010.01)
H01M 4/58 (2010.01) ***H01M 10/0566*** (2010.01)

(21) **International Application Number**:
PCT/JP2013/061961

(22) **International Filing Date**:
17 April 2013 (17.04.2013)

(25) **Filing Language**: English

(26) **Publication Language**: English

(30) **Priority Data**:

13/449,195	17 April 2012 (17.04.2012)	US
13/523,694	14 June 2012 (14.06.2012)	US

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(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

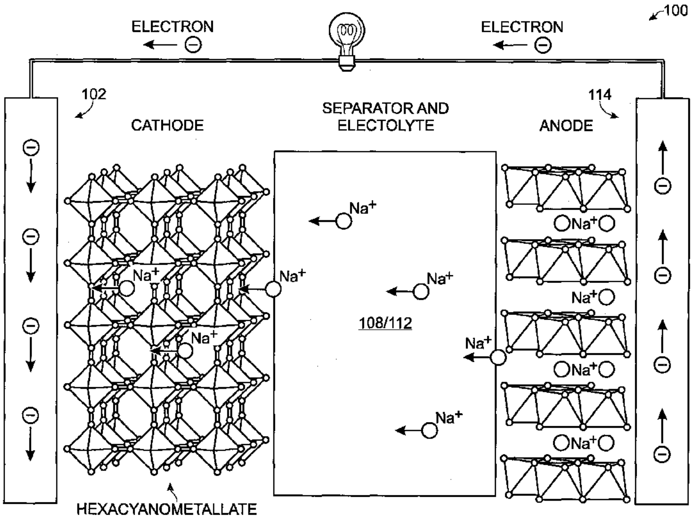
(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

(54) **Title**: ALKALI AND ALKALINE-EARTH ION BATTERIES WITH HEXACYANOMETALLATE CATHODE AND NON-METAL ANODE

FIG. 4



(57) **Abstract**: A battery structure is provided for making alkali ion and alkaline-earth ion batteries. The battery has a hexacyanometallate cathode, a non-metal anode, and non-aqueous electrolyte. A method is provided for forming the hexacyanometallate battery cathode and non-metal battery anode prior to the battery assembly. The cathode includes hexacyanometallate particles overlying a current collector. The hexacyanometallate particles have the chemical formula $A'_{n'}A_mM1_xM2_y(CN)_6$, and have a Prussian Blue hexacyanometallate crystal structure. The hexacyanometallate particles can be in a form of carbon-hexacyanometallate particles.

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DESCRIPTION

Title of Invention

ALKALI AND ALKALINE-EARTH ION BATTERIES WITH HEXACYANOMETALLATE CATHODE AND NON-METAL ANODE

Technical Field

This invention generally relates to electrochemical cells and, more particularly, to an alkali or alkaline-earth ion battery made from a hexacyanometallate cathode and non-metal anode.

This invention also relates to electrochemical cells and, more particularly, to method for forming a carbon-hexacyanometallate battery electrode.

Background Art

A battery is an electrochemical cell through which chemical energy and electric energy can be converted back and forth. The energy density of a battery is determined by its voltage and charge capacity. Lithium has the most negative potential of -3.04 V vs. H_2/H^+, and has the highest gravimetric capacity of 3860 milli-amp-hours per gram (mAh/g). Due to their high energy densities, lithium-ion batteries have led the portable electronics revolution. However, the high cost of lithium metal renders doubtful the commercialization of lithium batteries as large scale energy storage devices. Further, the demand for lithium and its reserve as a mineral have raised the need to build other types metal-ion batteries as an alternative.

Lithium-ion (Li-ion) batteries employ lithium storage compounds as the positive (cathode) and negative (anode) electrode materials. As a battery is cycled, lithium ions (Li^+) exchange between the positive and negative electrodes. Li-ion batteries have been referred to as rocking chair batteries because the lithium ions "rock" back and forth between the positive and negative electrodes as the cells are charged and discharged. The positive electrode (cathode) materials is typically a metal oxide with a layered structure, such as lithium cobalt oxide ($LiCoO_2$), or a material having a tunneled structure, such as lithium manganese oxide ($LiMn_2O_4$), on an aluminum current collector. The negative electrode (anode) material is typically a graphitic carbon, also a layered material, on a copper current collector. In the charge-discharge process, lithium ions are inserted into, or extracted from interstitial spaces of the active materials.

Similar to the lithium-ion batteries, metal-ion batteries use the metal-ion host compounds as their electrode materials in which metal-ions can move easily and reversibly. As for a Li^+-ion, it has one of the smallest radii of all metal ions and is compatible with the interstitial spaces of many materials, such as the layered $LiCoO_2$, olivine-structured $LiFePO_4$, spinel-structured $LiMn_2O_4$, and so on. Other metal ions, such as Na^+, K^+, Mg^{2+}, Al^{3+}, Zn^{2+}, etc., with large sizes, severely distort Li-based intercalation compounds and ruin their structures in several charge/discharge cycles. Therefore, new materials with large interstitial spaces would have to be used to host such metal-ions in a metal-ion battery.

Fig. 1 depicts the framework for an electrode material with large interstitial spaces in a metal-ion battery (prior art). It is inevitable that the large interstitial spaces in these materials readily absorb water molecules and impure ions, as shown. Water molecules also occupy lattices positions in the electrode material. Although these open spaces are very suitable for the intercalation of metal-ions with large sizes, the water molecules and impure ions degrade the electrochemical performance. In this example, Prussian blue analogues (PBs) with cubic/tetragonal/hexagonal framework have open "zeolytic" lattices that permit Na^+/K^+ -ions to move easily and reversibly in the framework.

Fig. 2 demonstrates the crystal structure of Prussian blue and its analogues (prior art). Their general molecular formula is $AM1M2(CN)_6 .zH_2O$, in which tetrahedrally coordinated A site is an alkali or alkaline-earth ion, and M1 and M2 are metal ions. The M1 and M2 metals are arranged in a three-dimensional checkerboard pattern and shown in a two-dimensional pattern. The crystal structure is analogous to that of the ABX_3 perovskite. M1 and M2 metal ions are in ordered arrangement on the B sites. The M1 ions are octahedrally coordinated to the nitrogen ends of the CN^- groups, and the M2 ions to their carbon ends. The M1 and M2 ions are connected by the C≡N to form the Prussian blue framework with large interstitial spaces.

The ratio of M1 and M2 may be an arbitrary number. The cyanide ligands (C≡N) octahedrally coordinate M1 and M2 to constitute a cubic framework that has a large interstitial space. The metal-ions or molecules of 'A' can locate in the interstitial space and balance the local charge. Although the molecular ratio for A:M1:M1:H_2O in Prussian blue and its analogues is not precisely 1:1:1:0, the general molecular formula of $AM1M2(CN)_6$ is used herein for simplicity. The typical compounds of $AM1M2(CN)_6$ include Prussian white ($K_2Fe(II)Fe(II)(CN)_6$), Prussian blue ($KFe(II)Fe(III)(CN)_6$), Berlin green ($Fe(III)Fe(III)(CN)_6$) and their analogues. The bond dipole moment of C≡N is around 3.0 Debye, which makes the ordering of the M1 and M2 ions with different spin-states in the framework. The material of $AM1M2(CN)_6$ has demonstrated a variety of interesting functions in optics, magnetic, and electrochemistry.

In an electrochemical cell with $AM1M2(CN)_6$ as an electrode component, the electrochemical reaction can take place only if (1) a redox couple is in the structure, (2) ions can transport in/out of the structure, and (3) electrons can transport to balance the charge neutrality. For example, the electrochemical reaction taking place in Prussian blue can be expressed as follows:

$KFe(II)Fe(III)(CN)_6 + K^+ + e^- \rightarrow K_2Fe(II)Fe(II)(CN)_6$.

In Prussian blue, the redox couple is Fe^{2+}/Fe^{3+}. In the reduction reaction, the Fe^{3+} ion obtains an electron and reduces to Fe^{2+}, and a potassium-ion moves to the interstitial space of the compound to balance the charge. Once the ion diffusion or electron conduction becomes very slow, the reaction voltage departs from equilibrium (overpotential) and gives $V = V_{eq} - V_{over}$, in which 'V_{eq}' is the equilibrium potential of the electrochemical reaction and 'V_{over}' is the overpotential. Slower ion or electron transport leads to a high overpotential and a low reaction voltage. For a battery, its energy is $E = V \times I = (V_{eq} - V_{over}) \times I$, where 'I' is the current. A large overpotential and small current lead to the poor performance of the electrochemical reaction.

The $AM1M2(CN)_6$ material has a large interstitial space in which ions can easily move in and out of the lattice. Ion transport is not a limiting factor affecting the kinetic parameters of the electrochemical reaction. On the other hand, $AM1M2(CN)_6$ has a wide band gap between the valence and conduction bands. This means that the $AM1M2(CN)_6$ is a very poor electronic conductor. The dried Prussian blue, for example, is an insulator, and Prussian white and Berlin green are semiconductors. The slow electronic transport along the skeleton of M1-N≡C-M2 results in poor electrochemical performance in a system containing $AM1M2(CN)_6$.

The large interstitial sites may host the large sized alkali or alkaline-earth ions (A). Water molecules may also occupy lattice positions in the PB analogues. The ion channels connecting the interstitial sites are similar in size to solvated alkali ions such as sodium, potassium, and alkaline-earth ions such as magnesium and calcium, allowing rapid transport of these ions throughout the lattice. Therefore, PB is a good choice for an electrode material in sodium/potassium/magnesium/calcium-ion batteries. Nonetheless, thermogravimetric analysis (TG) suggests that every PB molecule contains four to six water molecules. The occupation of water and impure ions in these materials definitely reduces the spaces to host the metal-ions and leads to the reduced capacity of these electrode materials. Therefore, $KCuFe(CN)_6$ has a theoretical capacity of 85.2 mAh/g, but its practical capacity is smaller than 60 mAh/g. In addition, water may react with the intercalated metal-ions and decrease the coulombic and energy efficiencies of the metal-ion batteries. Up to now, no method has been reported to remove the water and impure ions from the large interstitial spaces and lattice positions of the hexacyanometallate electrode materials for metal-ions batteries. As a result, most metal-ions batteries with a hexacyanometallate electrode use an aqueous solution as an electrolyte. These batteries have small specific capacities and low voltages.

The open framework structure of the transition metal hexacyanometallates offers a faster and reversible intercalation process for alkali and alkaline-earth ions (A_x). In a metal-ion battery structure, the metal ions need to be stored in either the anode or cathode electrode before assembly. In the case of a Li-ion battery with $LiCoO_2$, $LiFePO_4$, and $LiMn_2O_4$ cathodes, the Li ions are stored in the cathode and the anode is carbon. Therefore, these batteries are assembled in a discharged state. These batteries need to be run through a charge cycle, to move the Li ions to the carbon anode, before they have any power for discharge. In the case of Li-S, Li-air and Na-S batteries, the metal ions are stored in anode. Actually, these anodes are made of Li and Na metals. These batteries are assembled in the charged state - meaning the battery can discharge immediately after assembly. Since alkali (e.g., Li, Na, and

K), and other alkaline-earth (e.g., Mg and Ca) metals are very reactive with water vapor and oxygen, the manufacturing cost for such a battery would be prohibitively high, as the manufacturing has to be done in controlled environment.

In the case of sodium-ion batteries and potassium-ion batteries with hexacyanometallates $AM1M2(CN)_6$ as the cathode materials, it is easy to use a metal anode for the metal-ion battery. For example, a Na-ion battery can be made of a sodium anode and $KFe_2(CN)_6$ cathode, or a K-ion battery with potassium anode and $KFe_2(CN)_6$ cathode. However, these batteries must be assembled in controlled environment (H_2O-free, oxygen-free) if a metal anode is used.

It would be advantageous if alkali and alkaline-earth ion batteries could be made with a hexacyanometallate $A_xM1M2(CN)_6$ cathode and a non-metal anode.

It would be advantageous if electron transport could be improved in a $AM1M2(CN)_6$ battery electrode.

Summary of Invention

Described herein is an alkali-ion battery (e.g., a sodium-ion battery or potassium-ion battery) with a cathode of $A_xM1M2(CN)_6$, where the A cations may be Na or K, for example, where x = 0-2 and the anode is a non-metal. Also disclosed is an alkaline-earth-ion battery (e.g., a magnesium-ion battery or calcium-ion battery) with a cathode of $A_xM1M2(CN)_6$, where the A cations are Mg or Ca, for example, where x = 0-1 and the anode is a non-metal. The non-metal materials for the negative electrode (anode) include carbonaceous materials, oxides, sulfide, and so on.

The battery demonstrates high energy, long cycling life and low cost. Also disclosed is a process of forming an electrode that acts as an ion-source for hexacyanometallates, initially without sodium or potassium ions. A non-aqueous, polymer, or solid electrolyte can be used in the battery. M1 and M2 are the same or different metal ions. Some examples of M1 and M2 are as follows: M1, M2 = Ti, V, Cr, Mn, Fe, Co Ni, Cu, Zn, Ca, Mg, etc. The ratio of M1 and M2 can be an arbitrary number. The battery demonstrates a high voltage due to the use of a non-aqueous electrolyte.

Accordingly, a method is provided for forming a hexacyanometallate battery cathode. The method provides dried hexacyanometallate particles having a chemical formula $A'_nM1_xM2_y(CN)_6$ with a Prussian Blue hexacyanometallate crystal structure, including impurities and H2O. A' is an alkali or alkaline-earth cation. M1 is a metal with 2+ or 3+ valance positions. Likewise, M2 is a metal with 2+ or 3+ valance positions. (n) is in the range of 0.5 to 2, x is in the range of 0.5 to 1.5, and y is in the range of 0.5 to 1.5. The hexacyanometallate particles are mixed with a binder and electronic conductor powder in a low boiling point solvent. Drying the mixture forms a $A'_nM1_xM2_y(CN)_6$ paste. A metal current collector is coated with the paste, forming a cathode. After drying the paste, the cathode is soaked in an organic first electrolyte including a salt with alkali or alkaline-earth cations, and a first electric field is created in the first electrolyte between the cathode and a first counter electrode. In response to the first electric field, the method simultaneously removes A' cations, impurities, and water molecules from interstitial spaces and lattice positions in the Prussian Blue hexacyanometallate crystal structure. Hexacyanometallate particles, having a chemical formula of $A'_{n'}M1_xM2_y(CN)_6$, where $n' < n$, are formed overlying the cathode.

The method then soaks the cathode in an organic second electrolyte including a salt with A cations, where A is an alkali or alkaline-earth cation. In response to creating a second electric field in the second electrolyte between the cathode and a second counter electrode including A elements, A cations are added into the interstitial spaces of the $A'_{n'}M1_xM2_y(CN)_6$ crystal structure. As a result, a cathode is formed with hexacyanometallate particles having the chemical formula $A'_{n'}A_mM1_xM2_y(CN)_6$, where m is in a range of 0.5 to 2.

Additional details of the above-described method and a battery with a hexacyanometallate cathode and non-metal anode are presented below.

Described herein is a method to reduce the electron transport path in $AM1M2(CN)_6$ materials and to improve its performance in electrochemical applications. The method produces uniform and small size particles of $AM1M2(CN)_6$ material, making it a better electrical conductor. The method also reduces overpotential and increases the current for the electrochemical reaction of $AM1M2(CN)_6$.

Accordingly, a method is provided for forming a carbon-hexacyanometallate battery electrode. The method adds conducting carbon during the synthesis of hexacyanometallate. Carbon-hexacyanometallate ($AM1M2(CN)_6$) structures are collected, washed in deionized water, and then dried. In one aspect, adding carbon during the synthesis of hexacyanometallate includes: combining conducting carbon with a potassium ferricyanide solution, forming a first solution; stirring the first solution; preparing a Fe2+ solution; combining the Fe^{2+} solution with the first solution, forming a second solution; and, stirring the second solution. The collecting carbon-hexacyanometallate ($AM1_xM2_y(CN)_6$) structures are collected from the second solution.

The method may include the following additional steps. The carbon-hexacyanometallate structures are mixed with a binder and electronic conductor powder in a low boiling point solvent, forming a carbon-$AM1M2(CN)_6$ paste. A metal current collector is coated with the paste, and the paste is then dried to form an electrode.

Additional details of the above-described method are described below, along with an intimately contacting carbon-hexacyanometallate structure for battery electrode applications, and other methods for forming a carbon-hexacyanometallate battery electrode.

Brief Description of Drawings

Fig. 1 depicts the framework for an electrode material with large interstitial spaces in a metal-ion battery (prior art).

Fig. 2 demonstrates the crystal structure of Prussian blue and its analogues (prior art).

Fig. 3 is a partial cross-sectional view of a battery with a hexacyanometallate cathode and non-metal anode.

Fig. 4 is a partial cross-sectional schematic view of a Na-ion battery in the discharge state, with a $Na_xM1M2(CN)_6$ positive electrode and a non-metal negative electrode separated by a Na^+-ion permeable membrane.

Figs. 5A through 5C depict three types of battery configurations.

Fig. 6 is a flowchart illustrating a method for forming a hexacyanometallate battery cathode.

Fig. 7 is a flowchart illustrating a method for forming a non-metal battery anode.

Figs. 8A and 8B are schematic drawings depicting different variations of an intimately contacting carbon-hexacyanometallate structure for battery electrode applications.

Figs. 9A and 9B are drawings contrasting electron transport in uncoated and conductor-coated $AM1M2(CN)_6$ particles.

Fig. 10 is a schematic drawing depicting a one-step hexacyanometallate coating method during $AM1M2(CN)_6$ synthesis.

Fig. 11 is a drawing depicting a conducting film coating on $AM1M1(CN)_6$ particles.

Fig. 12 is a flowchart illustrating method for forming a carbon-hexacyanometallate battery electrode in which $KFe(II)Fe(III)(CN)_6$ is used as an example.

Fig. 13 is a flowchart illustrating an alternate method for forming a carbon-hexacyanometallate battery electrode.

Fig. 14 is a flowchart illustrating another variation of a method for forming a carbon-hexacyanometallate battery electrode.

Figs. 15A and 15B are scanning electron microscope (SEM) images of $KNiFe(CN)_6$.

Figs. 16A and 16B depict, respectively, the charge and discharge behavior of the two batteries.

Description of Embodiments

[EMBODIMENT 1]

Fig. 3 is a partial cross-sectional view of a battery with a hexacyanometallate cathode and non-metal anode. The battery 100 comprises a cathode 102 with hexacyanometallate particles 104 overlying a current collector 106. The hexacyanometallate particles 104 have the chemical formula $A'_{n'}A_mM1_xM2_y(CN)_6$, and have a Prussian Blue hexacyanometallate crystal structure (see Fig. 2). The A cations may be either alkali or alkaline-earth cations. Likewise, the A' cations may be either alkali or alkaline-earth cations. For example, the A and A' cations may be Na^+, K^+, Mg^{2+}, or Ca^{2+}. Note: the A and A' cations may be the same or a different material.

M1 is a metal with 2+ or 3+ valance positions. Likewise, M2 is a metal with 2+ or 3+ valance positions. For example, the M1 and M2 metals may be Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ca, or Mg. The M1 metal may be the same metal as the M2 metal, or a different metal than the M2 metal.

From the hexacyanometallate formula above, m is in the range of 0.5 to 2, x is in the range of 0.5 to 1.5, y is in the range of 0.5 to 1.5, and n' is in the range of 0 to 2. In one aspect, the cathode hexacyanometallate particles 104 have the chemical formula $A_mM1_xM2_y(CN)_6$, where n' = 0.

The battery 100 further comprises an electrolyte 108 capable of conducting A cations 110. An ion-permeable membrane 112 separates a non-metal anode 114 from the cathode 102. Some examples of anode materials include carbonaceous materials, oxides, sulfides, nitrides, silicon, composite material including metal nanoparticles with carbonaceous materials, and silicon nanostructures with carbonaceous materials. The electrolyte 108 may be a non-aqueous, organic, gel, polymer, solid electrolyte, or aqueous electrolyte.

In one example of the battery, the A cations are Na^+ cations, the ion permeable membrane 112 is a Na^+-ion permeable membrane, and the electrolyte 108 is a Na^+ soluble non-aqueous electrolyte. The general expression for the cathode may be: $Na_2M1M2(CN)_6$, $NaM1M2(CN)_6$, $NaKM1M2(CN)_6$, or $M1M2(CN)_6$. M1, M2 = Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ca, Mg, etc. The ratio of M1 and M2 can be an arbitrary number. For example: $Na_2Fe_2(CN)_6$, $NaFe_2(CN)_6$, $NaKFe_2(CN)_6$, and $Fe_2(CN)_6$.

In another example, the A cations are K^+ cations, the ion permeable membrane 112 is a K^+-ion permeable membrane, and the electrolyte 108 is a K+ soluble non-aqueous electrolyte. The general expression for the cathode materials may be: $K_2M1M2(CN)_6$, $KM1M2(CN)_6$, $NaKM1M2(CN)_6$, or $M1M2(CN)_6$. M1, M2 = Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ca, Mg, etc. The ratio of M1 and M2 can be an arbitrary number. For example: $K_2Fe_2(CN)_6$, $KFe_2(CN)_6$, and $NaKFe_2(CN)_6$.

In another example, the A cations are Mg^{2+} cations, the ion permeable membrane 112 is a Mg^{2+}-ion permeable membrane, and the electrolyte 108 is a Mg^{2+} soluble non-aqueous electrolyte. The general expression for the cathode materials may be: $MgM1M2(CN)_6$, $Mg_{0.5}M1M2(CN)_6$, or $M1M2(CN)_6$. M1, M2 = Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ca, Mg, etc. The ratio of M1 and M2 can be an arbitrary number. For example: $MgFe_2(CN)_6$, $Mg_{0.5}Fe_2(CN)_6$, or $Fe_2(CN)_6$.

If the A cations are Ca^{2+} cations, the ion permeable membrane 112 is a Ca^{2+}-ion permeable membrane, and the electrolyte 108 is a Ca^{2+} soluble non-aqueous electrolyte. The general expression for the Ca-ion battery is the same as the Mg-ion battery, just replacing Mg with Ca in the formulas above.

In one aspect, the cathode hexacyanometallate particles 104 have the chemical formula $A'_{n'}M1_xM2_y(CN)_6$, where m = 0. The anode 114 includes A cations, and the ion-permeable membrane 112 is permeable to A cations. More explicitly, the ion-permeable membrane 112 is permeable to the A cations used in the anode 114. As used herein, an anode is defined as being a non-metal anode if it is a composite material that includes a metal.

Thus, sodium-ion, potassium-ion, magnesium-ion, and calcium-ion batteries are disclosed with positive (cathode) electrodes of $A_xM1M2(CN)_6$, negative (anode) electrodes of a non-metal material, an ion-permeable membrane separating the cathode and anode, and an electrolyte. The material, $A_xM1M2(CN)_6$, demonstrates a framework that consists of a M1-N-C-M2 skeleton and large interstitial space as shown in Fig. 2. M1 and M2 are the same or different metal ions (M1, M2 = Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ca, Mg, etc.) and their ratio can be an arbitrary number. A-ions (Na, K, Mg and Ca) can easily and reversibly move in the interstitial space. The anode is a non-metal material. It can be one of carbonaceous materials, oxides, sulfides or nitrides. In order to obtain a high voltage for the battery, a non-aqueous electrolyte, such as organic electrolyte, gel electrolyte, polymer electrolyte, solid electrolyte, etc., may be used in the battery.

Fig. 4 is a partial cross-sectional schematic view of a Na-ion battery in the discharge state, with a $Na_xM1M2(CN)_6$ positive electrode 102 and a non-metal negative electrode 114 separated by a Na^+-ion permeable membrane 112. In order to obtain a high voltage, a Na^+ soluble non-aqueous solution 108, polymer, or solid electrolyte is used in the Na-ion battery. The non-metal negative electrode 114 is the carbonaceous material, oxide, sulfide, and so on. In the charge/discharge process, Na^+ ions “rock” back and forth between the positive electrode 102 and negative electrode 114. Similarly, a K-ion battery would have of $K_xM1M2(CN)_6$ positive electrode, a non-metal negative electrode, and a K^+-ion permeable membrane separating the cathode and anode electrodes. The battery charge reactions at the cathode and anode are shown below.

For sodium-ion battery, the positive electrode:

$Na_xM1M2(CN)_6 \rightarrow xNa^+ + M1M2(CN)_6 + xe^-$; and,

the negative electrode:

$Na^+ + e^- + \square \rightarrow (Na)\,\square$; $\square$ = non-metal negative electrode material.

For potassium-ion battery, the positive electrode:

$K_xM1M2(CN)_6 \rightarrow xK^+ + M1M2(CN)_6 + xe^-$; and,

the negative electrode:

$K^+ + e^- + \square \rightarrow (K)\,\square$; $\square$ = non-metal negative electrode material.

For magnesium-ion battery, the positive electrode:

$Mg_xM1M2(CN)_6 \rightarrow xMg^{2+} + M1M2(CN)_6 + 2xe^-$; and,

the negative electrode:

$Mg^{2+} + 2e^- + \square \rightarrow (Mg)\,\square$; $\square$ = non-metal negative electrode material.

For calcium-ion battery, the positive electrode:

$Ca_xM1M2(CN)_6 \rightarrow xCa^{2+} + M1M2(CN)_6 + 2xe^-$; and,

the negative electrode:

$Ca^{2+} + 2e^- + \square \rightarrow (Ca)\,\square$; $\square$ = non-metal negative electrode material.

In the discharge process, all reactions take place in the reverse direction.

The positive electrode fabrication process flow is as follows. Dried $A'_nM1M2(CN)_6$ (A' = Na, K, Mg, or Ca) powder with a particle size of 5 nm - 1 μm is mixed with binder, such as polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), etc., and an electronic conductor powder, in a low boiling point solvent to form a paste. The electronic conductor powder may be carbon black, carbon nanotube, carbon nanowire, grapheme, etc., with particle size of 5 nm - 10 μm. The $A'_nM1M2(CN)_6$ (A' = Na, K, Mg, or Ca) powder contains crystal water even after the drying process. The water is not shown in the formula. The composition of the paste is 60 wt.% - 95 wt.% $A'_nM1M2(CN)_6$, 0 wt.% - 30 wt.% electronic conductor powder, and 1wt.% - 15 wt.% binder. The paste is coated on a metal foil or mesh (Al, Ti, etc.) that is used as the current collector for the positive electrode. After drying, the electrode undergoes forming process. The forming process includes two steps: the first step is to remove the ions (A'_n) and residual water from the $A'_nM1M2(CN)_6$ lattice. The second step is to fill Na-ions, K-ions, Mg-ions, or Ca-ions into the $A'_nM1M2(CN)_6$ lattice. The Na ions and K ions (Mg ions and Ca ions) occupy the A site and these ions are moved in/out of the $A'_nA_mM1M2(CN)_6$ lattice during the discharge/charge cycles. Additional details of the 2-step forming process are provided in parent application entitled, ELECTRODE FORMING PROCESS FOR METAL-ION BATTERY WITH HEXACYANOMETALLATE ELECTRODE, invented by Yuhao Lu et al., Serial No. 13/432,993.

The forming process can be summarized as follows. For simplicity, it is assumed that the ions at the A site are all removed in the first step.

In the first step:

$A'_nM1M2(CN)_6 \rightarrow nA' + M1M2(CN)_6 + ne^-$;

Residual water is removed: $2H_2O = 4H+ + O_2\uparrow + 4e^-$.

In the second step:

$M1M2(CN)_6 + me^- + mNa^+ \rightarrow Na_mM1M2(CN)_6$ ($m \geqq 1$) for the sodium-ion battery; or,

$M1M2(CN)_6 + me^- + mK^+ \rightarrow K_mM1M2(CN)_6$ ($m \geqq 1$) for the potassium-ion battery; or,

$M1M2(CN)_6 + 2me^- + mMg^{2+} \rightarrow Mg_mM1M2(CN)_6$ ($m \geqq 0.5$) for the magnesium-ion battery; or,

$M1M2(CN)_6 + 2me^- + mCa^{2+} \rightarrow Ca_mM1M2(CN)_6$ ($m \geqq 0.5$) for the calcium-ion battery.

All steps are operated in a water-free environment. After the forming process, the electrode is ready for battery assembly.

Note that the A' ions in cathode material $A'_nM1M2(CN)_6$ before the forming process, and the A ions in $A_mM1M2(CN)_6$ after forming process may be a different material. For example, $K_xM1M2(CN)_6$ is used before the electrode forming process, and the materials change to $Na_xM1M2(CN)_6$ or $Na_xK_yM1M2(CN)_6$ after forming process for a Na-ion battery application.

The negative (anode) electrode is fabricated as follows. A dried non-metal negative electrode powder (e.g., carbonaceous material, oxides, or sulfides) is mixed with binder such as PTFE or PVDF, etc., and an electronic conductor powder (carbon black, carbon nanotube, carbon nanowire, grapheme, etc., with particle size of 5 nm - 10 µm) in low boiling point solvent to form a paste. The composition of the paste is 60 wt.% - 95 wt.% non-metal anode, 0 wt.% - 30 wt.% electronic conductor powder, and 1wt.% - 15 wt.% binder. The paste is coated on a metal foil or mesh (Cu, Ti, Ni, etc.) that is used as the current collector for the negative electrode. The negative electrode has a very low potential that can reduce the organic electrolyte to form an ion-permeable layer on the negative electrode so-called solid electrolyte interphase (SEI). The SEI improves the stability of the negative electrode in the ion battery. However, the reduction reaction exhausts the metal-ions (Na^+, K^+, Mg^{2+}, or Ca^{2+}) from the positive electrode, which decreases the capacity of the positive electrode. So a process of forming the electrode is applied to the negative electrode prior to the electrode slitting and battery assembly. The forming process is performed in a water-free environment. The negative electrode (anode) is paired with a counter metal-electrode (e.g., Na, K, Mg, Ca) in an electrochemical cell that includes an organic electrolyte with metal-ions (Na^+, K^+, Mg^{2+}, Ca^{2+}). Upon receiving the electrical field in the electrochemical cell that moves the metal ions toward the negative electrode, the metal-ions insert into or react with the negative electrode. At the same time, the electrolyte reacts with the negative electrode to form a SEI layer that contains metal ions, carbon, oxygen, and hydrogen on the negative electrode surface. Next, in the same electrochemical cell, an opposite electrical field is applied and the metal-ions are de-inserted from the negative electrode. However, the SEI layer is intact. For example, if a Na-ion battery is being formed, the counter electrode in made with Na, and the electrolyte includes Na ions. After the process, an-ion permeable inner layer forms on the electrode.

Figs. 5A through 5C depict three types of battery configurations. After the positive electrode and the negative electrode are prepared, the battery can be assembled. A membrane separates the positive and negative electrode. The membrane can be one of polymer, gel, or solid materials. The sandwich electrode assembly can be configured according to the container shape of the battery. The electrode assembly is put into a container. If a liquid solution is needed to help the ion transport, it can be injected into the container. After all the electrodes are thoroughly soaked in electrolyte, the container is sealed.

An all-solid sodium ion-battery or potassium-ion battery, uses a different composition for the electrode fabrication. The all-solid ion battery consists of the positive electrode and the negative electrode separated by an ion-conduct solid electrolyte. For example, in the sodium-ion battery, β-Al_2O_3, $NaZr_2(PO_4)_3$, $Na_4Zr_2(SiO_4)_3$ and their derivates can be used as the Na+-ion solid electrolyte. In order to improve the ions transport in the electrode, the 5wt.% - 60 wt.% solid electrolyte powder can be added into the pastes of the positive electrode and the negative electrode to prepare the electrode. After obtaining the electrode, they can be assembled into a battery as described above.

Fig. 6 is a flowchart illustrating a method for forming a hexacyanometallate battery cathode. Although the method is depicted as a sequence of numbered steps for clarity, the numbering does not necessarily dictate the order of the steps. It should be understood that some of these steps may be skipped, performed in parallel, or performed without the requirement of maintaining a strict order of sequence. Generally however, the method follows the numeric order of the depicted steps. The method starts at Step 600.

Step 602 provides dried hexacyanometallate particles having a chemical formula $A'_nM1_xM2_y(CN)_6$ with a Prussian Blue hexacyanometallate crystal structure, including impurities and H_2O. A' is either an alkali or alkaline-earth cations, and M1 is a metal with 2+ or 3+ valance positions. Likewise, M2 is a metal 2+ or 3+ valance positions, n is in the range of 0.5 to 2, x is in the range of 0.5 to 1.5, and y is in the range of 0.5 to 1.5. For example, the A' cations may be Na^+, K^+, Mg^{2+}, or Ca^{2+}. The M1 metal may be Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ca, or Mg for example. Likewise, the M2 metal may be Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ca, or Mg. The M1 may be the same metal as the M2 metal or a different metal than the M2 metal. The dried hexacyanometallate particles typically have a size in the range of 5 nm to 10 microns.

Step 604 mixes the hexacyanometallate particles with a binder and electronic conductor powder in a low boiling point solvent. Some examples of low boiling point solvents include amyl acetate, acetone, diethyl carbonate, dimethyl carbonate, and n-methyl-2-pyrrolidone (NMP). The binder may be PTFE or PVDF, for example. Typically, the electronic conductor powder is carbon black, carbon nanotubes, carbon nanowire, or grapheme, having a particle size in the range of 5 nm to 10 microns.

Step 606 dries the mixture, forming a $A'_nM1_xM2_y(CN)_6$ paste. In one aspect, the paste is 60 to 95 weight (wt) % $A'_nM1_xM2_y(CN)_6$, 0 to 30 wt % electronic conductor powder, and 1 to 15 wt % binder.

Step 608 coats a metal current collector with the paste, forming a cathode. Step 610 dries the paste. Step 612 soaks the cathode in an organic first electrolyte including a salt with either alkali or alkaline-earth cations. Step 614 accepts a first electric field in the first electrolyte between the cathode and a first counter electrode. In response to the first electric field, Step 616 simultaneously removes A' cations, impurities, and water molecules from interstitial spaces in the Prussian Blue hexacyanometallate crystal structure. Step 618 forms hexacyanometallate particles having a chemical formula of $A'_{n'}M1_xM2_y(CN)_6$, where $n' < n$, overlying the cathode.

In one aspect, subsequent to forming $A'_{n'}M1_xM2_y(CN)_6$ in Step 618, Step 620 soaks the cathode in an organic second electrolyte including a salt with A cations, where A is either an alkali or alkaline-earth cation. Typically, the A cations are Na^+, K^+, Mg^{2+}, or Ca^{2+}. The A cations may be the same material as the A' cations or a different material than the A' cations.

Step 622 accepts a second electric field in the second electrolyte between the cathode and a second counter electrode including A elements. In response to the second electric field, Step 624 adds A cations into the interstitial spaces of the $A'_{n'}M1_xM2_y(CN)_6$ crystal structure. Step 626 forms a cathode with hexacyanometallate particles having the chemical formula $A'_{n'}A_mM1_xM2_y(CN)_6$, where m is in a range of 0.5 to 2. In one aspect, Step 626 forms hexacyanometallate particles with the chemical formula of $A_mM1_xM2_y(CN)_6$, where $n' = 0$.

Fig. 7 is a flowchart illustrating a method for forming a non-metal battery anode. The method begins at Step 700. Step 702 provides a dried non-metal electrode powder. Step

704 mixes the dried non-metal electrode powder with a binder and an electronic conductor powder in a low boiling point solvent. Step 706 forms a paste. Step 708 coats a metal current collector with the paste, forming an anode. In Step 710 the paste dries. Step 712 soaks the anode in a first organic electrolyte including a salt with metal ions. Step 714 accepts a first electric field in the electrolyte between the anode and a metal first counter electrode. In response to the first electric field, Step 716 forms a metal solid electrolyte interphase (SEI) layer overlying the anode. In one aspect, the metal SEI layer additionally includes carbon, oxygen, hydrogen, and combinations of the above-mentioned elements.

Subsequent to forming the SEI layer, Step 718 accepts a second electric field, opposite in polarity to the first electric field between the anode and the first counter electrode. Step 720 removes metal ions from the anode while maintaining the SEI layers intact.

In one aspect, soaking the anode in the first organic electrolyte in Step 712 includes soaking in a first organic electrolyte with A cations such as Na, K, Mg, or Ca. Likewise, Step 714 uses a metal first counter electrode that additional includes the A cations used in Step 712. Then, Step 716 forms the anode from a composite that includes the A cations used in Steps 712 and 714.

A battery with a hexacyanometallate cathode and non-metal anode has been provided with an associated cathode fabrication process. Examples of particular materials and process steps have been presented to illustrate the invention. However, the invention is not limited to merely these examples. Other variations and embodiments of the invention will occur to those skilled in the art.

[EMBODIMENT 2]

Figs. 8A and 8B are schematic drawings depicting different variations of an intimately contacting carbon-hexacyanometallate structure for battery electrode applications. The structure 300' comprises carbon (C) 302' and hexacyanometallate particles 304'. A bond exists between the carbon 302' and the hexacyanometallate particles 304' that may be either a physical bond, caused by electrostatic attraction, or a chemical bond, caused by chemical reactions. From the hexacyanometallate formula $AM1_xM2_y(CN)_6$, x is in the range of 0.5 to 1.5, and y is in the range of 0.5 to 1.5.

The carbon 302' may take the form of particles having a size in the range of 10 nanometers (nm) to 20 microns, a carbon sheet, graphene, nanoparticles (less than 10 nm), nanotubes, or wires. As in the conventional meaning of the word, a nanotube has a hollow center axis The hexacyanometallate particles 304' is smaller than the carbon 302', with a size in a range of 10 nm to 10 microns.

Fig. 8A depicts a plurality of hexacyanometallate particles bonded to each carbon form. Fig. 8B depicts a plurality of carbon forms bonded to each hexacyanometallate particle.

Conventionally, there are three steps for battery electrode fabrication. The first step is to fabricate the particles for battery electrode. In the case of $AM1M2(CN)_6$ particles, this includes precipitation of $AM1M2(CN)_6$ particles after mixing the $M1^{n+}$ ($n = 2$ or 3) solution and $[M2(CN)_6]^{m-}$ ($m= 3$ or 4) solution. The second step is to mix the $AM1M2(CN)_6$ particles with conductive carbon particles and organic binders (polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), etc.) in a low boiling point solvent to form a paste. The mixing can be done by adding together all components and mixing them in a ball mill jar. The third step is to coat the paste on a metal foil as the current collector. After the drying process, the electrode can be used in electrochemical cell. However, since the particles are very small, the conductive carbon particles do not totally cover the $AM1M2(CN)_6$ particle.

In order to form the C-$AM1M2(CN)_6$ intimate contact, and to improve the electron conduction, the carbon can be added and forms intimate contact to $AM1M2(CN)_6$ in three scenarios: during the $AM1M2(CN)_6$ synthesis, after $AM1M2(CN)_6$ particle formation and prior to the electrode printing, and after the electrode formation and drying. Figs. 9A through 11 describe processes for forming C-$AM1M2(CN)_6$ intimate contact.

Fig. 10 is a schematic drawing depicting a one-step hexacyanometallate coating method during $AM1M2(CN)_6$ synthesis. An electronic conductor, for example graphene or other carbonaceous material, is dispersed in a reactant solution. In general, the electronic conductor has a large surface area to which a soluble reactant can be uniformly adsorbed. The reactants are dropped into a reactor very slowly with a strong stirring. After the reaction, $AM1M2(CN)_6$ with a small particle size uniformly forms on the surface of the electronic conductor. In the synthesis of the Prussian blue, for example, the reaction can be simply expressed as:

$Fe^{2+} + Fe(CN)_6^{3-}\text{-}\square + K^+ \rightarrow KFe(II)Fe(III)(CN)_6\text{-}\square$;

where □ is the electronic conductor.

More explicitly, a carbon black (surface area: 10 - 100 m^2/g) is dispersed in a potassium ferricyanide solution (its concentration can be controlled at 0.0005M - 0.5 M). The ratio of potassium ferricyanide to carbon black is determined by its application. In one example, the ratio is 80:20. A water-soluble surfactant can be added into the solution in order to obtain a uniform carbon suspension. After two-hours of ultrasonic stirring, the solution is poured into a burette. In the other burette, a Fe^{2+} solution is prepared. The mole ration of Fe^{2+} to ferricyanide is 2:1. The two solutions are dripped into a beaker very slowly with strong stirring. After the solutions completely drip off, the beaker is still kept stirring for 5 hours. The product in the beaker is filtered or centrifuged. After at least three washes in deionized water, the product is dried in a vacuum drier overnight.

Figs. 15A and 15B are scanning electron microscope (SEM) images of $KNiFe(CN)_6$. As an example, $KNiFe(CN)_6$ was synthesized with carbon black using the above-described method. Fig. 15A shows $KNiFe(CN)_6$ particles uniformly coated on the surface with carbon powder. The carbon black not only improves the electronic conductivity of $KNiFe(CN)_6$, but it also favors the small and uniform $KNiFe(CN)_6$ particle formation. The electrical performance of the battery made of C-$KNiFe(CN)_6$ particles was compared to the battery made of $KNiFe(CN)_6$ particles. Fig. 15B is a more detailed image of a carbon particle.

Figs. 16A and 16B depict, respectively, the charge and discharge behavior of the two batteries. For the battery made of C-$KNiFe(CN)_6$ particles (modified), small particle size and better conductivity improves the utilization of the electrode materials and increases specific capacities, as compared to the battery made of (as-synthesized) $KNiFe(CN)_6$ particles. The discharge capacity of electrode made of C-$KNiFe(CN)_6$ particles is about 60 mAh/g, but that of pure $KNiFe(CN)_6$ is smaller than 30 mAh/g. In addition, the battery made of C-$KNiFe(CN)_6$ particles demonstrates a capacity of about 40 mAh/g at the 1C charge rate. With the same conditions, the battery made of pure $KNiFe(CN)_6$ shows a very low capacity.

Fig. 11 is a drawing depicting a conducting film coating on $AM1M1(CN)_6$ particles. The C-$AM1M2(CN)_6$ intimate contact can be formed after $AM1M2(CN)_6$ particle synthesis, but prior to the to the electrode printing. Small particles of $AM1M2(CN)_6$ 304' can be synthesized with the reaction of $M1^{n+}$ (n = 2 or 3) and $[M2(CN)_6]^{m-}$ (m= 3 or 4) ions. Once the particles of $AM1M2(CN)_6$ are obtained, a layer of electronic conductor, such as carbon 302', can be coated on their surface using physical or chemical methods. For example, atomic layer deposition (ALD), physical vapor deposition (PVD), chemical vapor deposition (CVD), hydrothermal synthesis, or ball milling method, etc., can be used to coat the layer of electronic conductor. However, two problems are worth noting. One is that some electronic conductors have very high reductive activity, for example, carbonaceous materials that can reduce M1 and M2 from the high valence to the low valence. For example, in the process of using the hydrothermal method to coat the carbon layer on the surface of $KFe(II)Fe(III)(CN)_6$, the material can be reduced to $K_2Fe(II)Fe(II)(CN)_6$.

The other problem is the selection of the electronic conductor for the coating. After the coating process, the electronic conductor layer is covered on the particles uniformly. For the electrochemical reaction to occur on the $AM1M2(CN)_6$, the layer of the electronic conductor must be ‘A’ ion-permeable. In other words, the layer of the electronic conductor cannot retard the ‘A’ ion transport between the $AM1M2(CN)_6$ particle and the electrolyte. In some cases, the conducting film 302’ does not have to be continuous so that $AM1M2(CN)_6$ particles have direct contact to the electrolyte and “A” ions are readily intercalating/deintecalating to the $AM1M2(CN)_6$ particles.

9A and 9B are drawings contrasting electron transport in uncoated and conductor-coated $AM1M2(CN)_6$ particles. In this aspect the conducting film can be deposited after the electrode formation. Obtaining small and uniformly distributed particle is a step to improving the electronic transport in the $AM1M2(CN)_6$. For clarity, an electrode 400’ (cathode) is shown with only one $AM1M2(CN)_6$ particle 304’. In a small $AM1M2(CN)_6$ particle, the transport path between an electron 402’ and ions 404’ is shortened. The ion (A^+)

404' conduction is through an electrolyte surrounding the $AM1M2(CN)_6$ particle. After going into the $AM1M2(CN)_6$ lattice, the A^+ ions 404' move through the large interstitial sites in a direction towards a more negative potential. On the other hand, the electron 402' is moving within the $AM1M2(CN)_6$ material. The electron 402' movement in the $AM1M2(CN)_6$ particle 404' is basically governed by the electron conductivity behavior of the $AM1M2(CN)_6$ material. It is known that $AM1M2(CN)_6$ has low electron conductivity, which results in a slow electrochemical reaction. To improve the electron conductivity of $AM1M2(CN)_6$ electrode, it is possible to coat a good electronic conductor 406' on the $AM1M2(CN)_6$ surface. One example of good electronic conductor is carbon. The electronic conductor 406' provides a highway for the fast electrons transport as shown in Fig. 9B. In the reduction reaction of $AM1M2(CN)_6$, 'A'-ions diffuse to the reactive place 408' along the interstitial space, but electrons 402' can move to reactive place along the external electronic conductor 406'. Therefore, the electrochemical reaction has a small overpotential and a large current.

The A cations may be either alkali or alkaline-earth cations. For example, the A cations may be Na^+, K^+, Mg^{2+}, or Ca^{2+}. M1 is a metal with 2+ or 3+ valance positions. Likewise, M2 is a metal with 2+ or 3+ valance positions.

For example, the M1 and M2 metals may be Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ca, or Mg. The M1 metal may be the same metal as the M2 metal, or a different metal than the M2 metal.

Fig. 12 is a flowchart illustrating method for forming a carbon-hexacyanometallate battery electrode in which $KFe(II)Fe(III)(CN)_6$ is used as an example. Although the method is depicted as a sequence of numbered steps for clarity, the numbering does not necessarily dictate the order of the steps. It should be understood that some of these steps may be skipped, performed in parallel, or performed without the requirement of maintaining a strict order of sequence. Generally however, the method follows the numeric order of the depicted steps. The method starts at Step 700'.

Step 702' adds conducting carbon during the synthesis of hexacyanometallate. The conducting carbon can be the form of a particle having a size in a range of 10 nm to 20 microns, a carbon sheet, graphene, nonoparticles, nanotubes, or wires. Step 704' collects carbon-hexacyanometallate ($AM1M2(CN)_6$) structures. Step 706' washes the carbon-hexacyanometallate structures in deionized water. Step 708' dries the carbon-hexacyanometallate structures. Step 710' mixes the carbon-hexacyanometallate structures with a binder and electronic conductor powder in a low boiling point solvent. Step 712' forms a carbon-$AM1M2(CN)_6$ paste. Step 714' coats a metal current collector with the paste. Step 716' dries the paste to form an electrode.

In one aspect, adding carbon during the synthesis of hexacyanometallate in Step 702' includes substeps. Step 702'a combines conducting carbon with a potassium ferricyanide solution, forming a first solution. Step 702'b stirs the first solution. Step 702'c prepares a Fe^{2+} solution. Step 702'd combines the Fe^{2+} solution with the first solution, forming a second solution. Step 702'e stirs the second solution. Then, Step 704' includes collecting carbon-hexacyanometallate ($AM1M2(CN)_6$) structures from the second solution. In one aspect, the combination of Steps 702'a and 702'e form a specific $AM1M2(CN)_6$ material, which may be $KFeFe(CN)_6$ for example. Other methods of enabling Step 702' would be known in the art.

Step 712' may form a carbon-$AM1M2(CN)_6$ paste with a plurality of hexacyanometallate particles bonded to each carbon form, where the bond is a physical bond or a chemical bond. Alternatively, Step 712' may form the carbon-$AM1M2(CN)_6$ paste with a plurality of carbon forms bonded (chemical or physical) to each hexacyanometallate particle. Either way, Step 712' forms the carbon-

AM1M2$(CN)_6$ paste with hexacyanometallate particles have a size in the range of 10 nm to 10 microns.

Fig. 13 is a flowchart illustrating an alternate method for forming a carbon-hexacyanometallate battery electrode. The method begins at Step 800'. Step 802' forms hexacyanometallate particles. In one aspect, the hexacyanometallate particles have a size in the range of 10 nm to 10 microns. The hexacyanometallate particles may be formed using one of the following processes: template, hydrothermal, co-deposition, or sonochemical synthesis.

Step 804' coats the hexacyanometallate particles with a conducting carbon. The conducting carbon may be in the form of particles having a size in the range of 10 nm to 20 microns, a carbon sheet, graphene, nanoparticles, nanotubes, or wires. The coating may be performed using one of the following processes: atomic layer deposition (ALD), physical vapor deposition (PVD), chemical vapor deposition (CVD), hydrothermal synthesis, or ball milling. Step 806' forms carbon-hexacyanometallate structures. Step 808' mixes the carbon-hexacyanometallate structures with a binder and electronic conductor powder in a low boiling point solvent. Step 810' forms a carbon-AM1M2$(CN)_6$ paste. Step 812' coats a metal current collector with the paste. Step 814' dries the paste to form an electrode.

In one aspect, forming the carbon-$AM1M2(CN)_6$ paste in Step 810' includes forming a paste with a plurality of carbon atoms bonded to each hexacyanometallate molecule, where the bond is a physical bond or a chemical bond.

Fig. 14 is a flowchart illustrating another variation of a method for forming a carbon-hexacyanometallate battery electrode. The method begins at Step 900'. Step 902' forms hexacyanometallate particles. In one aspect, the hexacyanometallate particles have a size in the range of 10 nm to 10 microns. Step 904' mixes the hexacyanometallate particles with a binder and electronic conductor powder in a low boiling point solvent. Step 906' forms a carbon-$AM1M2(CN)_6$ paste. Step 908' coats a metal current collector with the paste. Step 910' dries the paste to form an electrode. Step 912' coats the electrode with a layer of conducing materials.

In one aspect, coating the electrode with the layer of conducting materials in Step 912' includes using a deposition process such as CVD, vapor phase ALD, or liquid phase coating. In another aspect, Step 912' uses a conducting material having a thickness in the range from 0.5 nm to 20 nm, where the material is either carbon or a metal material. The C-$AM1M2(CN)_6$ in the conducting material coating the electrode includes carbon that either fully covers or partially covers the $AM1M2(CN)_6$ particle surfaces.

Methods have been provided for forming a carbon-hexacyanometallate battery electrode, as well as a carbon-hexacyanometallate structure. Examples of particular materials and process steps have been presented to illustrate the invention. However, the invention is not limited to merely these examples. Other variations and embodiments of the invention will occur to those skilled in the art.

"ALKALI AND ALKALINE-EARTH ION BATTERIES WITH HEXACYANOMETALLATE CATHODE AND NON-METAL ANODE, invented by Yuhao Lu et al., Serial No. 13/449,195, filed April 17, 2012, attorney docket no. SLA3151" and "ELECTRODE FORMING PROCESS FOR METAL-ION BATTERY WITH HEXACYANOMETALLATE ELECTRODE, invented by Yuhao Lu et al., Serial No. 13/432,993, filed March 28, 2012, attorney docket no. SLA3146" are incorporated herein by reference.

This invention can be also constructed as below.

(1) A battery with a hexacyanometallate cathode and non-metal anode, the battery comprising:

a cathode with hexacyanometallate particles overlying a current collector, the hexacyanometallate particles having a chemical formula $A'_{n'}A_mM1_xM2_y(CN)_6$, and having a Prussian Blue hexacyanometallate crystal structure,

where A cations are selected from a group consisting of alkali and alkaline-earth cations;

where A' cations are selected from a group consisting of alkali and alkaline-earth cations;

where M1 is a metal selected from a group consisting of 2+ and 3+ valance positions;

where M2 is a metal selected from a group consisting of 2+ and 3+ valance positions;

where m is in a range of 0.5 to 2;

where x is in a range of 0.5 to 1.5;

where y is in a range of 0.5 to 1.5;

where n' is in a range of 0 to 2;

an electrolyte capable of conducting A cations;

a non-metal anode; and,

an ion-permeable membrane separating the anode from the cathode.

(2) The battery of (1) wherein A cations are selected from a first group consisting of Na^+, K^+, Mg^{2+}, and Ca^{2+}; and,

wherein A' cations are selected from a first group consisting of Na^+, K^+, Mg^{2+}, and Ca^{2+}.

(3) The battery of (1) wherein the M1 metal is selected from a group consisting of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ca, and Mg; and,

wherein the M2 metal is selected from a group consisting of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ca, and Mg.

(4) The battery of (1) wherein the M1 metal is selected from a group consisting of the same metal as the M2 metal and a different metal than the M2 metal.

(5) The battery of (1) wherein the anode material is selected from a group consisting of carbonaceous materials, oxides, sulfides, nitrides, silicon, composite material including metal nanoparticles with carbonaceous materials, and silicon nanostructures with carbonaceous materials.

(6) The battery of (1) wherein the electrolyte is selected from a group consisting of non-aqueous, organic, gel, polymer, solid electrolyte, and aqueous electrolytes.

(7) The battery of (1) wherein the A cations are Na^+ cations;

wherein the ion permeable membrane is a Na^+-ion permeable membrane; and,

wherein the electrolyte is a Na^+ soluble non-aqueous electrolyte.

(8) The battery of (1) wherein the A cations are K^+ cations;

wherein the ion permeable membrane is a K^+-ion permeable membrane; and,

wherein the electrolyte is a K^+ soluble non-aqueous electrolyte.

(9) The battery of (1) wherein the A cations are Mg^{2+} cations;

wherein the ion permeable membrane is a Mg^{2+}-ion permeable membrane; and,

wherein the electrolyte is a Mg^{2+} soluble non-aqueous electrolyte.

(10) The battery of (1) wherein the A cations are Ca^{2+} cations;

wherein the ion permeable membrane is a Ca^{2+}-ion permeable membrane; and,

wherein the electrolyte is a Ca^{2+} soluble non-aqueous electrolyte.

(11) The battery of (1) wherein A cations are selected from a group consisting of the same material as the A' cations and a different material than the A' cations.

(12) The battery of (1) wherein the cathode hexacyanometallate particles have the chemical formula $A_mM1_xM2_y(CN)_6$, where n' = 0.

(13) The battery of (1) wherein the cathode hexacyanometallate particles have the chemical formula $A'_{n'}M1_xM2_y(CN)_6$, where m = 0;

wherein the anode includes A cations; and,

wherein the ion-permeable membrane is permeable to A cations.

(14) A method for forming a hexacyanometallate battery cathode, the method comprising:

providing dried hexacyanometallate particles having a chemical formula $A'_nM1_xM2_y(CN)_6$ with a Prussian Blue hexacyanometallate crystal structure, including impurities and H_2O;

where A' is selected from a group consisting of alkali and alkaline-earth cations;

where M1 is a metal selected from a group consisting of 2+ and 3+ valance positions;

where M2 is a metal selected from a group consisting of 2+ and 3+ valance positions;

where n is in a range of 0.5 to 2;

where x is in a range of 0.5 to 1.5;

where y is in a range of 0.5 to 1.5;

mixing the hexacyanometallate particles with a binder and electronic conductor powder in a low boiling point solvent;

drying the mixture, forming a $A'_nM1_xM2_y(CN)_6$ paste;

coating a metal current collector with the paste, forming a cathode;

drying the paste;

soaking the cathode in an organic first electrolyte including a salt selected from the group consisting of alkali and alkaline-earth cations;

accepting a first electric field in the first electrolyte between the cathode and a first counter electrode;

in response to the first electric field, simultaneously removing A' cations, impurities, and water molecules from interstitial spaces in the Prussian Blue hexacyanometallate crystal structure; and,

forming hexacyanometallate particles having a chemical formula of $A'_{n'}M1_xM2_y(CN)_6$, where $n' < n$, overlying the cathode.

(15) The method of (14) further comprising:

subsequent to forming $A'_{n'}M1_xM2_y(CN)_6$, soaking the cathode in an organic second electrolyte including a salt with A cations, where A is selected from a group consisting of alkali and alkaline-earth cations;

accepting a second electric field in the second electrolyte between the cathode and a second counter electrode including A elements;

in response to the second electric field, adding A cations into the interstitial spaces of the $A'_{n'}M1_xM2_y(CN)_6$ crystal structure; and,

forming a cathode with hexacyanometallate particles having the chemical formula $A'_{n'}A_mM1_xM2_y(CN)_6$, where m is in a range of 0.5 to 2.

(16) The method of (15) wherein soaking the cathode in the second electrolyte including a salt with A cations

includes the A cations being selected from a group consisting the same material as the A' cations and a different material than the A' cations.

(17) The method of (14) wherein the A' cations are selected from a group consisting of Na^+, K^+, Mg^{2+}, and Ca^{2+}.

(18) The method of (15) wherein the A cations are selected from a group consisting of Na^+, K^+, Mg^{2+}, and Ca^{2+}.

(19) The method of (14) wherein the M1 metal is selected from a group consisting of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ca, and Mg; and,

wherein the M2 metal is selected from a group consisting of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ca, and Mg.

(20) The method of (14) wherein the M1 metal is selected from a group consisting of the same metal as the M2 metal and a different metal than the M2 metal.

(21) The method of (14) wherein providing the dried hexacyanometallate particles includes providing particles having a size in a range of 5 nanometers (nm) to 10 microns.

(22) The method of (14) wherein mixing the hexacyanometallate particles with the binder and electronic conductor powder includes mixing with a binder selected from a group consisting of polytetrafluoroethylene (PTFE) and PVDF.

(23) The method of (14) wherein mixing the hexacyanometallate particles with the binder and electronic

conductor powder includes mixing with an electronic conductor powder selected from a group consisting of carbon black, carbon nanotubes, carbon nanowire, and grapheme, having a particle size in a range of 5 nm to 10 microns.

(24) The method of (14) wherein forming the $A'_nM1_xM2_y(CN)_6$ paste includes forming a paste with 60 to 95 weight (wt) % $A'_nM1_xM2_y(CN)_6$, 0 to 30 wt % electronic conductor powder, and 1 to 15 wt % binder.

(25) The method of (15) wherein forming hexacyanometallate particles having a chemical formula of $A_mA'_{n'}M1_xM2_y(CN)_6$ includes forming hexacyanometallate particles with the chemical formula of $A_mM1_xM2_y(CN)_6$, where n' = 0.

(26) A method for forming a non-metal battery anode, the method comprising:

providing a dried non-metal electrode powder;

mixing the dried non-metal electrode powder with a binder and an electronic conductor powder in a low boiling point solvent;

forming a paste;

coating a metal current collector with the paste, forming an anode;

drying the paste;

soaking the anode in a first organic electrolyte including a salt with metal ions;

accepting a first electric field in the electrolyte between the anode and a metal first counter electrode; and,

in response to the first electric field, forming a metal solid electrolyte interphase (SEI) layer overlying the anode.

(27) The method of (26) further comprising:

subsequent to forming the SEI layer, accepting a second electric field, opposite in polarity to the first electric field between the anode and the first counter electrode; and,

removing metal ions from the anode while maintaining the SEI layers intact.

(28) The method of (26) wherein soaking the anode in the first organic electrolyte includes the metal ions being selected from a group consisting of Na, K, Mg, and Ca; and,

wherein accepting the first electric field includes accepting the electrolyte between the anode and a first counter electrode with the selected metal ions.

(29) The method of (26) wherein forming the metal SEI layer overlying the anode includes forming an SEI with additional elements selected from a group consisting of carbon, oxygen, hydrogen, and combinations of the above-mentioned elements.

(30) The method of (26) wherein soaking the anode in the first organic electrolyte includes soaking in a first

organic electrolyte with A cations selected from a group consisting of Na, Ka, Mg, and Ca;

wherein accepting the first electric field includes accepting the first electric field between the anode and a metal first counter electrode additional with the selected A cations; and,

wherein forming the metal SEI layer includes additionally forming the anode from a composite with the selected A cations.

(31) A method for forming a carbon-hexacyanometallate battery electrode, the method comprising:

adding conducting carbon during the synthesis of hexacyanometallate;

collecting carbon-hexacyanometallate ($AM1M2(CN)_6$) structures;

washing the carbon-hexacyanometallate structures in deionized water; and,

drying the carbon-hexacyanometallate structures.

(32) The method of (31) wherein adding carbon during the synthesis of hexacyanometallate includes:

combining conducting carbon with a potassium ferricyanide solution, forming a first solution;

stirring the first solution;

preparing a Fe^{2+} solution;

combining the Fe^{2+} solution with the first solution, forming a second solution;

stirring the second solution; and,

wherein collecting carbon-hexacyanometallate ($AM1M2(CN)_6$) structures includes collecting carbon-hexacyanometallate ($AM1M2(CN)_6$) structures from the second solution.

(33) The method of (31) further comprising:

mixing the carbon-hexacyanometallate structures with a binder and electronic conductor powder in a low boiling point solvent;

forming a carbon-$AM1M2(CN)_6$ paste;

coating a metal current collector with the paste; and,

drying the paste to form an electrode.

(34) The method of (31) wherein adding conducting carbon includes the conducting carbon being in a form selected from a group consisting of a particle having a size in a range of 10 nanometers (nm) to 20 microns, a carbon sheet, graphene, nonoparticles, nanotubes, and wires.

(35) The method of (34) wherein forming the carbon-$AM1M2(CN)_6$ paste includes forming a paste with a plurality of hexacyanometallate particles bonded to each carbon form, where the bond is selected from a group consisting of a physical bond and a chemical bond.

(36) The method of (33) wherein forming the carbon-$AM1M2(CN)_6$ paste includes forming a paste with a plurality of carbon forms bonded to each hexacyanometallate particle, where the bond is selected from a group consisting of a physical bond and a chemical bond.

(37) The method of (33) wherein forming the carbon-$AM1M2(CN)_6$ paste includes forming a paste with hexacyanometallate particles have a size in a range of 10 nm to 10 microns.

(38) An intimately contacting carbon-hexacyanometallate structure for battery electrode applications, the structure comprising:

carbon (C);

hexacyanometallate ($AM1M2(CN)_6$) particles; and,

a bond between the carbon and the hexacyanometallate particles, where a bond is selected from a group consisting of a physical and a chemical bond.

(39) The structure of (38) wherein the carbon is in a form selected from a group consisting of a particle having a size in a range of 10 nanometers (nm) to 20 microns, a carbon sheet, graphene, nanoparticles, nanotubes, and wires.

(40) The structure of (39) wherein a plurality of hexacyanometallate particles are bonded to each carbon form.

(41) The structure of (38) wherein a plurality of carbon forms are bonded to each hexacyanometallate particle.

(42) The structure of (38) where the hexacyanometallate particles is smaller than the carbon, with a size in a range of 10 nm to 10 microns.

(43) A method for forming a carbon-hexacyanometallate battery electrode, the method comprising:

forming hexacyanometallate ($AM1M2(CN)_6$) particles;

coating the hexacyanometallate particles with a conducting carbon; and,

forming carbon-$AM1M2(CN)_6$ structures.

(44) The method of (43) further comprising:

mixing the carbon-hexacyanometallate structures with a binder and electronic conductor powder in a low boiling point solvent;

forming a carbon-$AM1_xM2_y(CN)_6$ paste;

coating a metal current collector with the paste; and,

drying the paste to form an electrode.

(45) The method of (43) wherein coating the hexacyanometallate particles with the conducting carbon includes using conducting carbon in a form selected from a group consisting of a particle having a size in a range of 10 nanometers (nm) to 20 microns, a carbon sheet, graphene, nanoparticles, nanotubes, and wires.

(46) The method of (44) wherein forming the carbon-$AM1M2(CN)_6$ paste includes forming a paste with a plurality of carbon atoms bonded to each hexacyanometallate molecule, where the bond is selected from a group consisting of a physical bond and a chemical bond.

(47) The method of (43) wherein forming hexacyanometallate particles includes forming the hexacyanometallate particles using a process selected from a group consisting of template, hydrothermal, co-deposition, and sonochemical synthesis.

(48) The method of (43) wherein coating the hexacyanometallate particles with the conducting carbon includes using a process selected from a group consisting of atomic layer deposition (ALD), physical vapor deposition (PVD), chemical vapor deposition (CVD), hydrothermal synthesis, and ball milling.

(49) The method of (43) wherein forming hexacyanometallate particles includes forming hexacyanometallate particles having a size in a range of 10 nm to 10 microns.

(50) A method for forming a carbon-hexacyanometallate battery electrode, the method comprising:

forming hexacyanometallate particles;

mixing the hexacyanometallate particles with a binder and a conducting carbon powder in a low boiling point solvent;

forming a carbon-$AM1M2(CN)_6$ paste;

coating a metal current collector with the paste;

drying the paste to form an electrode; and,

coating the electrode with a layer of conducing materials.

(51) The method of (50) wherein coating the electrode with the layer of conducting materials includes using a deposition process selected from a group consisting of chemical vapor deposition (CVD), vapor phase atomic layer deposition (ALD), and liquid phase coating.

(52) The method of (50) wherein coating the electrode with the layer of conducting materials includes using a conducting material having a thickness in a range from 0.5 nanometers (nm) to 20 nm, where the material is selected from a group consisting of carbon (C) and a metal material.

(53) The method of (50) wherein coating the electrode with the layer of conducting materials includes coating with carbon in a manner selected from a group consisting of fully covering and partially covering the $AM1M2(CN)_6$ particle surfaces.

(54) The method of (50) wherein forming the hexacyanometallate particle includes forming

hexacyanometallate particles having a size in a range of 10 nm to 10 microns.

CLAIMS

1. A battery with a hexacyanometallate cathode and non-metal anode, the battery comprising:

a cathode with hexacyanometallate particles overlying a current collector, the hexacyanometallate particles having a chemical formula $A'_{n'}A_mM1_xM2_y(CN)_6$, and having a Prussian Blue hexacyanometallate crystal structure,

where A cations are selected from a group consisting of alkali and alkaline-earth cations;

where A' cations are selected from a group consisting of alkali and alkaline-earth cations;

where M1 is a metal selected from a group consisting of 2+ and 3+ valance positions;

where M2 is a metal selected from a group consisting of 2+ and 3+ valance positions;

where m is in a range of 0.5 to 2;

where x is in a range of 0.5 to 1.5;

where y is in a range of 0.5 to 1.5;

where n' is in a range of 0 to 2;

an electrolyte capable of conducting A cations;

a non-metal anode; and,

an ion-permeable membrane separating the anode from the cathode.

2. The battery of claim 1 wherein A cations are selected from a first group consisting of Na^+, K^+, Mg^{2+}, and Ca^{2+}; and,

wherein A' cations are selected from a first group consisting of Na^+, K^+, Mg^{2+}, and Ca^{2+}.

3. The battery of claim 1 wherein the M1 metal is selected from a group consisting of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ca, and Mg; and,

wherein the M2 metal is selected from a group consisting of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ca, and Mg.

4. The battery of claim 1 wherein the M1 metal is selected from a group consisting of the same metal as the M2 metal and a different metal than the M2 metal.

5. The battery of claim 1 wherein the anode material is selected from a group consisting of carbonaceous materials, oxides, sulfides, nitrides, silicon, composite material including metal nanoparticles with carbonaceous materials, and silicon nanostructures with carbonaceous materials.

6. The battery of claim 1 wherein the electrolyte is selected from a group consisting of non-aqueous, organic, gel, polymer, solid electrolyte, and aqueous electrolytes.

7. The battery of claim 1 wherein the A cations are Na^+ cations;

wherein the ion permeable membrane is a Na^+-ion permeable membrane; and,

wherein the electrolyte is a Na^+ soluble non-aqueous electrolyte.

8. The battery of claim 1 wherein the A cations are K^+ cations;

wherein the ion permeable membrane is a K^+-ion permeable membrane; and,

wherein the electrolyte is a K^+ soluble non-aqueous electrolyte.

9. The battery of claim 1 wherein the A cations are Mg^{2+} cations;

wherein the ion permeable membrane is a Mg^{2+}-ion permeable membrane; and,

wherein the electrolyte is a Mg^{2+} soluble non-aqueous electrolyte.

10. The battery of claim 1 wherein the A cations are Ca^{2+} cations;

wherein the ion permeable membrane is a Ca^{2+}-ion permeable membrane; and,

wherein the electrolyte is a Ca^{2+} soluble non-aqueous electrolyte.

11. The battery of claim 1 wherein A cations are selected from a group consisting of the same material as the A' cations and a different material than the A' cations.

12. The battery of claim 1 wherein the cathode hexacyanometallate particles have the chemical formula $A_mM1_xM2_y(CN)_6$, where n' = 0.

13. The battery of claim 1 wherein the cathode hexacyanometallate particles have the chemical formula $A'_{n'}M1_xM2_y(CN)_6$, where m = 0;

wherein the anode includes A cations; and,

wherein the ion-permeable membrane is permeable to A cations.

14. The battery of claim 1 wherein the battery comprises a carbon(C) bonded to the hexacyanometallate particles; and,

wherein a bond between the carbon(C) and the hexacyanometallate particles is selected from a group consisting of a physical and a chemical bond.

15. The battery of claim 14 wherein the carbon(C) is in a form selected from a group consisting of a particle having a size in a range of 10 nanometers (nm) to 20 microns, a carbon sheet, graphene, nanoparticles, nanotubes, and wires.

16. The battery of claim 15 wherein a plurality of hexacyanometallate particles are bonded to each carbon(C) form.

17. The battery of claim 15 wherein a plurality of carbon(C) forms are bonded to each hexacyanometallate particle.

18. The structure of claim 14 where the hexacyanometallate particles is smaller than the carbon(C), with a size in a range of 10 nm to 10 microns.

19. A method for forming a hexacyanometallate battery cathode, the method comprising:

providing dried hexacyanometallate particles having a chemical formula $A'_nM1_xM2_y(CN)_6$ with a Prussian Blue hexacyanometallate crystal structure, including impurities and H_2O;

where A' is selected from a group consisting of alkali and alkaline-earth cations;

where M1 is a metal selected from a group consisting of 2+ and 3+ valance positions;

where M2 is a metal selected from a group consisting of 2+ and 3+ valance positions;

where n is in a range of 0.5 to 2;

where x is in a range of 0.5 to 1.5;

where y is in a range of 0.5 to 1.5;

mixing the hexacyanometallate particles with a binder and electronic conductor powder in a low boiling point solvent;

drying the mixture, forming a $A'_nM1_xM2_y(CN)_6$ paste;

coating a metal current collector with the paste, forming a cathode;

drying the paste;

soaking the cathode in an organic first electrolyte including a salt selected from the group consisting of alkali and alkaline-earth cations;

accepting a first electric field in the first electrolyte between the cathode and a first counter electrode;

in response to the first electric field, simultaneously removing A' cations, impurities, and water molecules from interstitial spaces in the Prussian Blue hexacyanometallate crystal structure; and,

forming hexacyanometallate particles having a chemical formula of $A'_{n'}M1_xM2_y(CN)_6$, where $n' < n$, overlying the cathode.

20. The method of claim 19 further comprising:

subsequent to forming $A'_{n'}M1_xM2_y(CN)_6$, soaking the cathode in an organic second electrolyte including a salt with A cations, where A is selected from a group consisting of alkali and alkaline-earth cations;

accepting a second electric field in the second electrolyte between the cathode and a second counter electrode including A elements;

in response to the second electric field, adding A cations into the interstitial spaces of the $A'_{n'}M1_xM2_y(CN)_6$ crystal structure; and,

forming a cathode with hexacyanometallate particles having the chemical formula $A'_{n'}A_mM1xM2y(CN)_6$, where m is in a range of 0.5 to 2.

21. The method of claim 20 wherein soaking the cathode in the second electrolyte including a salt with A

cations includes the A cations being selected from a group consisting the same material as the A' cations and a different material than the A' cations.

22. The method of claim 19 wherein the A' cations are selected from a group consisting of Na^+, K^+, Mg^{2+}, and Ca^{2+}.

23. The method of claim 20 wherein the A cations are selected from a group consisting of Na^+, K^+, Mg^{2+}, and Ca^{2+}.

24. The method of claim 19 wherein the M1 metal is selected from a group consisting of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ca, and Mg; and,

wherein the M2 metal is selected from a group consisting of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ca, and Mg.

25. The method of claim 19 wherein the M1 metal is selected from a group consisting of the same metal as the M2 metal and a different metal than the M2 metal.

26. The method of claim 19 wherein providing the dried hexacyanometallate particles includes providing particles having a size in a range of 5 nanometers (nm) to 10 microns.

27. The method of claim 19 wherein mixing the hexacyanometallate particles with the binder and electronic conductor powder includes mixing with a binder selected from a group consisting of polytetrafluoroethylene (PTFE) and PVDF.

28. The method of claim 19 wherein mixing the hexacyanometallate particles with the binder and electronic conductor powder includes mixing with an electronic conductor powder selected from a group consisting of carbon black, carbon nanotubes, carbon nanowire, and grapheme, having a particle size in a range of 5 nm to 10 microns.

29. The method of claim 19 wherein forming the $A'_nM1_xM2_y(CN)_6$ paste includes forming a paste with 60 to 95 weight (wt) % $A'_nM1_xM2_y(CN)_6$, 0 to 30 wt % electronic conductor powder, and 1 to 15 wt % binder.

30. The method of claim 20 wherein forming hexacyanometallate particles having a chemical formula of $A_mA'_{n'}M1_xM2_y(CN)_6$ includes forming hexacyanometallate particles with the chemical formula of $A_mM1_xM2_y(CN)_6$, where n' = 0.

31. The method of claim 28 wherein coating the metal current collector with the paste, forming a cathode includes using a deposition process selected from a group consisting of chemical vapor deposition(CVD), vapor phase atomic layer deposition(ALD), and liquid phase coating.

32. The method of claim 28 wherein coating the metal current collector with the paste, forming a cathode includes coating with carbon in a manner selected from a group consisting of fully covering and partially covering the $A'_nM1_xM2_y(CN)_6$ particle surfaces.

33. The method of claim 19 wherein providing dried hexacyanometallate particles having a chemical formula $A'_nM1_xM2_y(CN)_6$ with a Prussian Blue hexacyanometallate crystal structure, including impurities and H_2O includes:

adding a conducting carbon during the synthesis of hexacyanometallate;

collecting carbon-hexacyanometallate($A'_nM1_xM2_y(CN)_6$) structures;

washing the carbon-hexacyanometallate($A'_nM1_xM2_y(CN)_6$) structures in deionized water; and,

drying the carbon-hexacyanometallate structures.

34. The method of claim 33 wherein adding the conducting carbon during the synthesis of hexacyanometallate includes:

combining conducting carbon with a potassium ferricyanide solution, forming a first solution;

strring the first solution;

preparing a Fe^{2+} solition;

combining the Fe^{2+} solution with the first solution, forming a second solution;

stirring the second solution; and,

wherein collecting the carbon-hexacyanometallate($A'_nM1_xM2_y(CN)_6$) structures includes collecting the carbon-hexacyanometallate($A'_nM1_xM2_y(CN)_6$) structures from the second solution.

35. The method of claim 33 wherein adding the conducting carbon during the synthesis of hexacyanometallate includes the conducting carbon being in a form selected from a group consisting of a particle having a size in a range of 10 nanometers(nm) to 20 microns, a carbon sheet, graphene, nanoparticles, nanotubes, and wires.

36. The method of claim 35 wherein forming the hexacyanometallate($A'_nM1_xM2_y(CN)_6$) paste includes forming

a paste with a plurality of hexacyanometallate particles bonded to each carbon form, where the bond is selected from a group consisting of physical bond and a chemical bond.

37. The method of claim 35 wherein forming the hexacyanometallate($A'_nM1_xM2_y(CN)_6$) paste includes forming a paste with a plurality of carbon forms bonded to each hexacyanometallate particle, where the bond is selected from a group consisting of physical bond and a chemical bond.

38. The method of claim 33 wherein forming the hexacyanometallate($A'_nM1_xM2_y(CN)_6$) paste includes forming a paste with hexacyanometallate particles have a size in a range of 10nm to 10 microns.

39. The method of claim 19 wherein providing dried hexacyanometallate particles having a chemical formula $A'_nM1_xM2_y(CN)_6$ with a Prussian Blue hexacyanometallate crystal structure, including impurities and H_2O includes:

forming hexacyanometallate($A'_nM1_xM2_y(CN)_6$) particles;

coating the hexacyanometallate($A'_nM1_xM2_y(CN)_6$) particles with a conducting carbon; and, forming carbon-hexacyanometallate($A'_nM1_xM2_y(CN)_6$) structures.

40. The method of claim 39 wherein coating the hexacyanometallate($A'_nM1_xM2_y(CN)_6$) particles with the conducting carbon includes using the conducting carbon in a form selected from a group consisting of a particle having a size in a range of 10 nanometers(nm) to 20 microns, a carbon sheet, graphene, nanoparticles nanotubes, and wires.

41. The method of claim 39 wherein forming the hexacyanometallate($A'_nM1_xM2_y(CN)_6$) paste includes forming a paste with a plurality of carbon atoms bonded to each hexacyanometallate molecules, where the bond is selected from a group consisting of physical bond and a chemical bond.

42. The method of claim 39 wherein forming hexacyanometallate($A'_nM1_xM2_y(CN)_6$) particles includes forming the hexacyanometallate($A'_nM1_xM2_y(CN)_6$) particles using a process selected from a group consisting of template, hydrothermal, co-deposition, and sonochemical synthesis.

43. The method of claim 39 wherein coating the hexacyanometallate($A'_nM1_xM2_y(CN)_6$) particles with the

conducting carbon includes using a process selected from a group consisting of atomic layer deposition(ALD), physical vapor deposition(PVD), chemical vapor deposition(CVD), hydrothermal synthesis, and ball milling.

44. The method of claim 39 wherein forming hexacyanometallate($A'_nM1_xM2_y(CN)_6$) particles includes forming the hexacyanometallate($A'_nM1_xM2_y(CN)_6$) particles having a size in a range of 10nm to 10 microns.

45. A method for forming a non-metal battery anode, the method comprising:

providing a dried non-metal electrode powder;

mixing the dried non-metal electrode powder with a binder and an electronic conductor powder in a low boiling point solvent;

forming a paste;

coating a metal current collector with the paste, forming an anode;

drying the paste;

soaking the anode in a first organic electrolyte including a salt with metal ions;

accepting a first electric field in the electrolyte between the anode and a metal first counter electrode; and, in response to the first electric field, forming a metal solid electrolyte interphase (SEI) layer overlying the anode.

46. The method of claim 45 further comprising:

subsequent to forming the SEI layer, accepting a second electric field, opposite in polarity to the first electric field between the anode and the first counter electrode; and,

removing metal ions from the anode while maintaining the SEI layers intact.

47. The method of claim 45 wherein soaking the anode in the first organic electrolyte includes the metal ions being selected from a group consisting of Na, K, Mg, and Ca; and,

wherein accepting the first electric field includes accepting the electrolyte between the anode and a first counter electrode with the selected metal ions.

48. The method of claim 45 wherein forming the metal SEI layer overlying the anode includes forming an SEI with additional elements selected from a group consisting of carbon, oxygen, hydrogen, and combinations of the above-mentioned elements.

49. The method of claim 45 wherein soaking the anode in the first organic electrolyte includes soaking in a first organic electrolyte with A cations selected from a group consisting of Na, Ka, Mg, and Ca;

wherein accepting the first electric field includes accepting the first electric field between the anode and a metal first counter electrode additional with the selected A cations; and,

wherein forming the metal SEI layer includes additionally forming the anode from a composite with the selected A cations.

FIG. 1

(PRIOR ART)

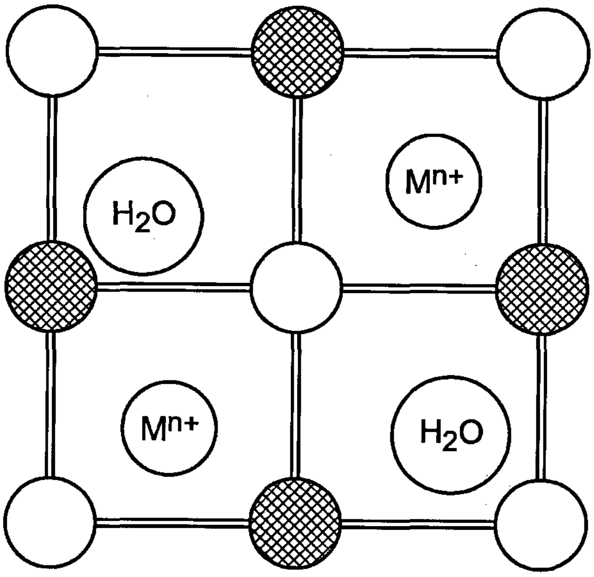


FIG. 2

(PRIOR ART)

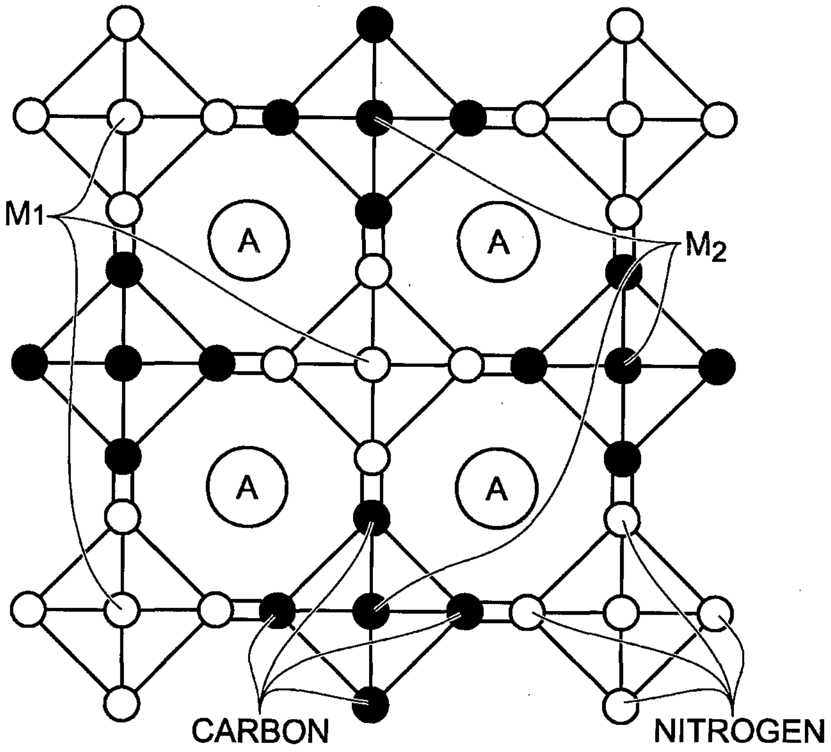
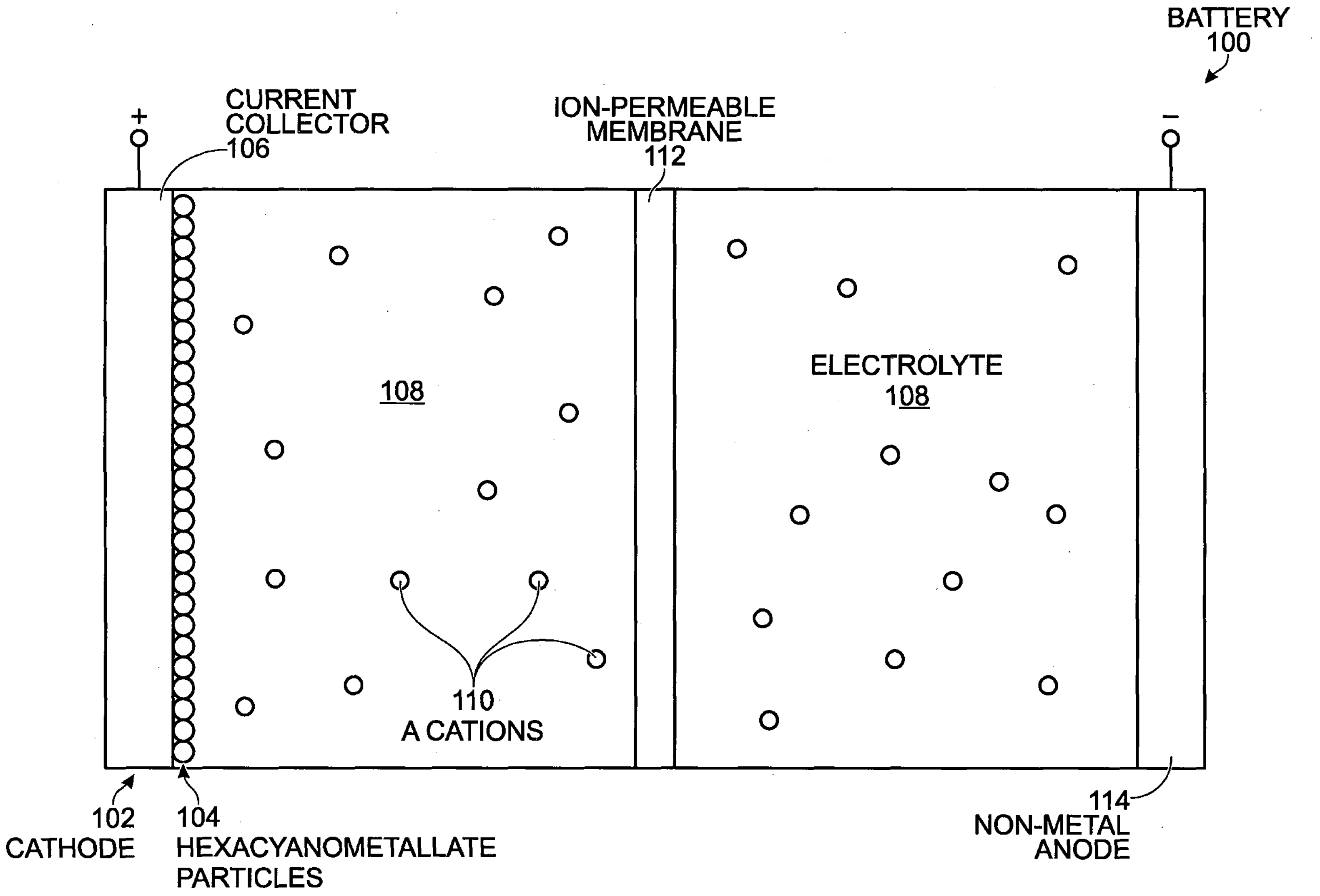


FIG. 3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+
−
CURRENT
COLLECTOR
106
ION-PERMEABLE
MEMBRANE
112
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ELECTROLYTE
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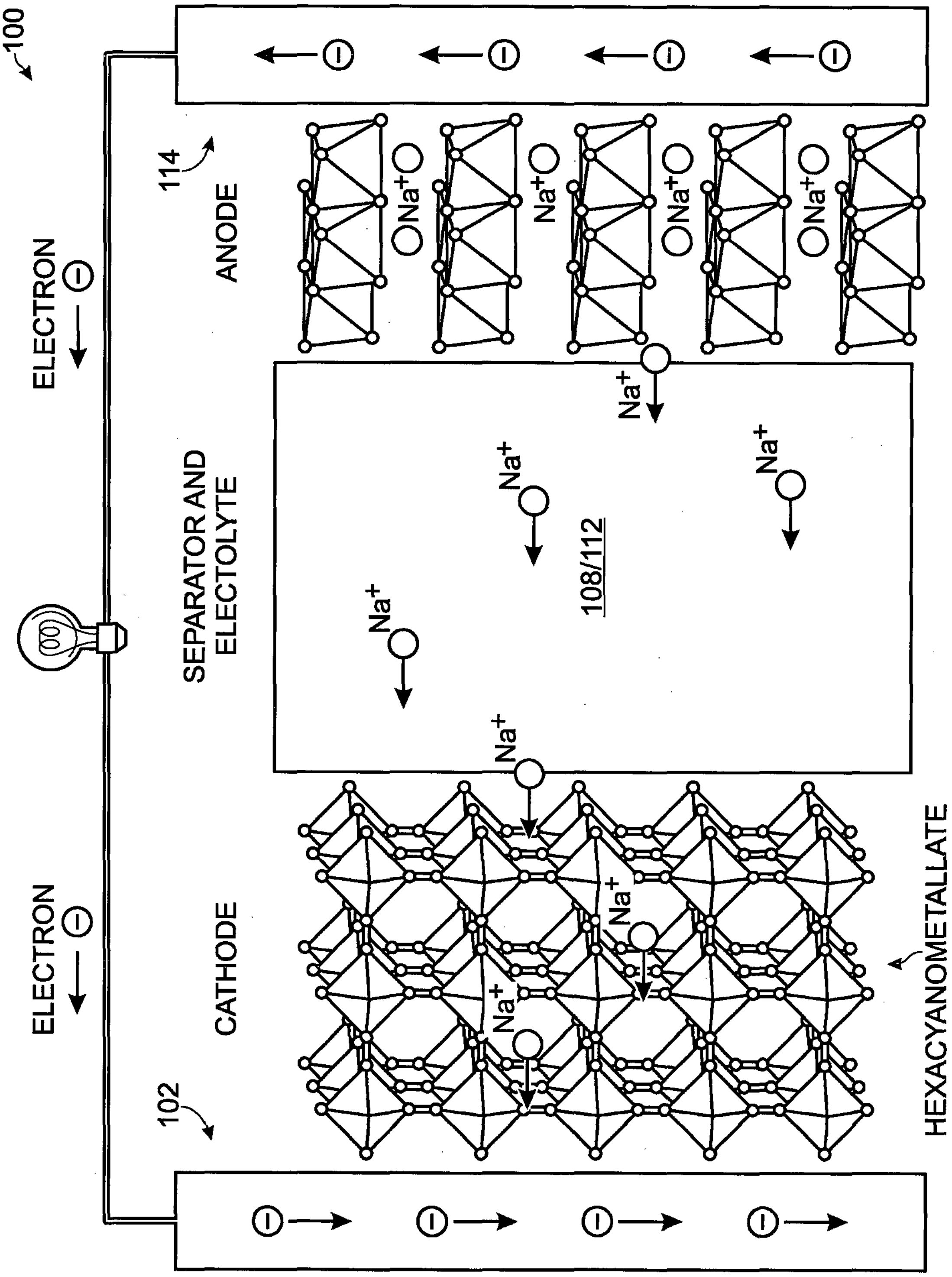
102
CATHODE
104
HEXACYANOMETALLATE
PARTICLES
114
NON-METAL
ANODE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ELECTRON
⊖
ELECTRON
⊖
ANODE
114
Na+
Na+
Na+
Na+
SEPARATOR AND ELECTOLYTE
108/112
Na+
Na+
Na+
Na+
Na+
CATHODE
102
Na+
Na+
HEXACYANOMETALLATE

FIG. 4

FIG. 5A

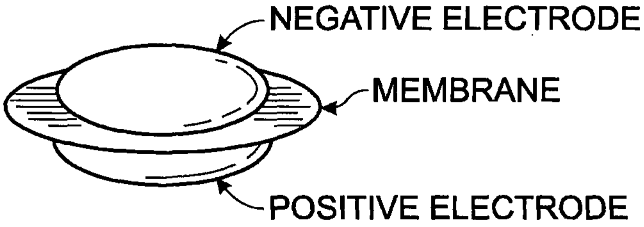


FIG. 5B

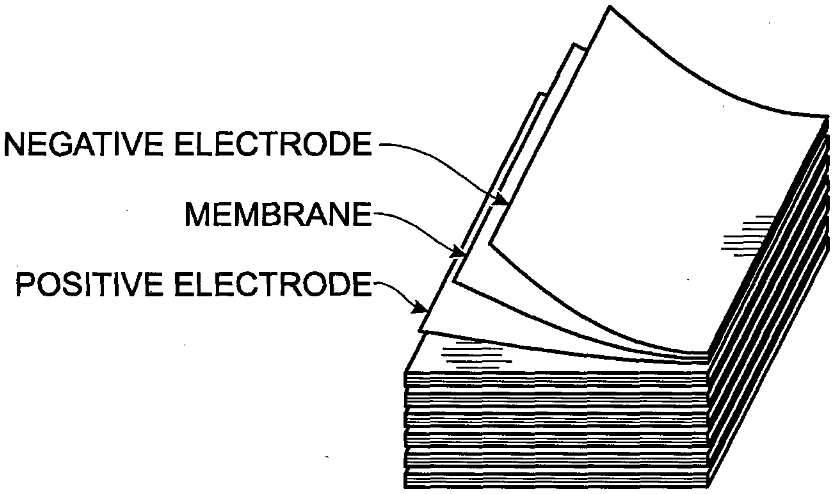


FIG. 5C

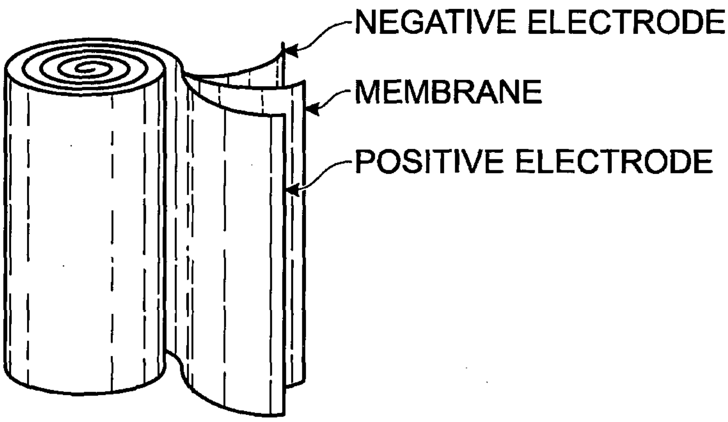


FIG. 6

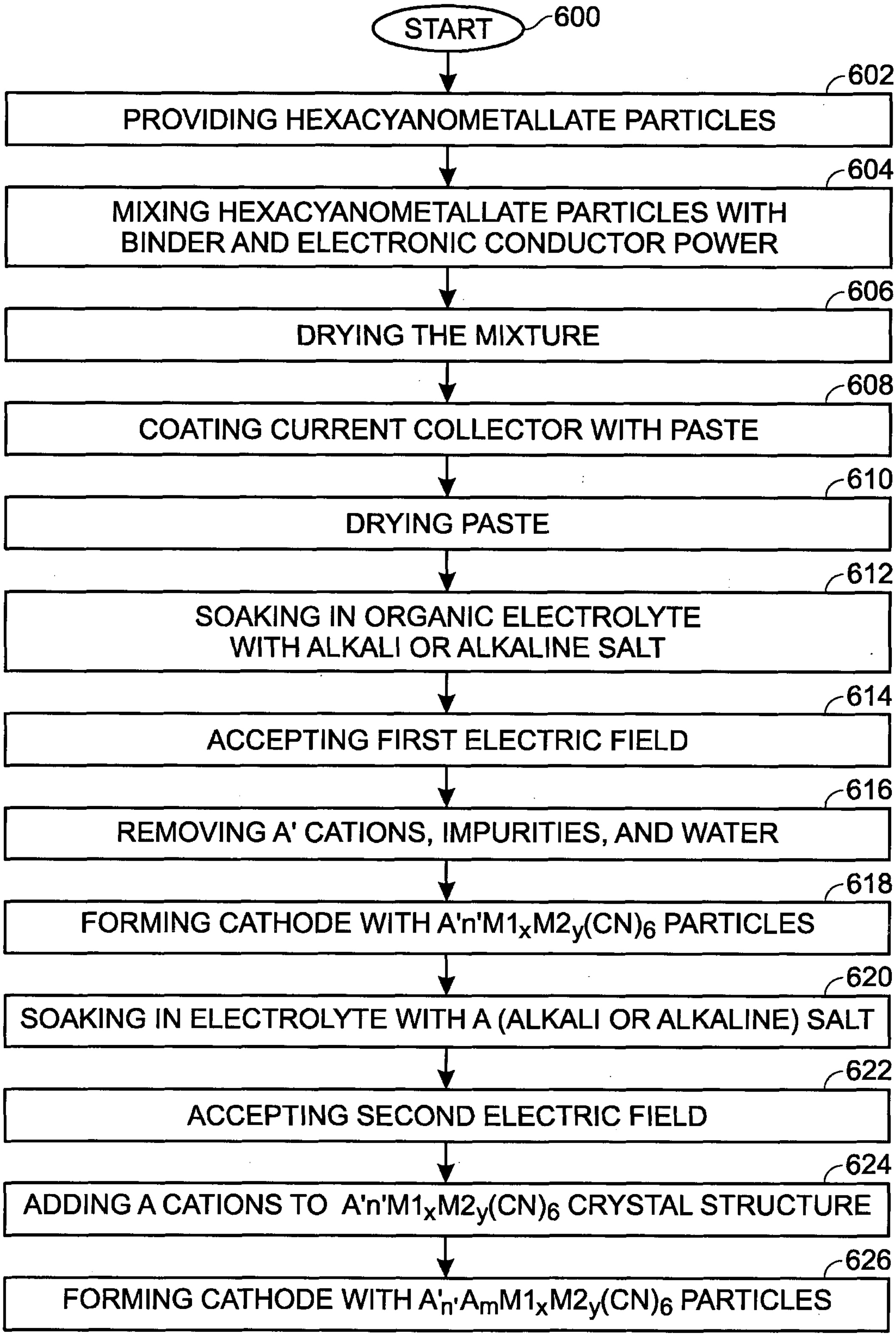

START
600
602
PROVIDING HEXACYANOMETALLATE PARTICLES
604
MIXING HEXACYANOMETALLATE PARTICLES WITH BINDER AND ELECTRONIC CONDUCTOR POWER
606
DRYING THE MIXTURE
608
COATING CURRENT COLLECTOR WITH PASTE
610
DRYING PASTE
612
SOAKING IN ORGANIC ELECTROLYTE WITH ALKALI OR ALKALINE SALT
614
ACCEPTING FIRST ELECTRIC FIELD
616
REMOVING A' CATIONS, IMPURITIES, AND WATER
618
FORMING CATHODE WITH A'n'$M1_xM2_y(CN)_6$ PARTICLES
620
SOAKING IN ELECTROLYTE WITH A (ALKALI OR ALKALINE) SALT
622
ACCEPTING SECOND ELECTRIC FIELD
624
ADDING A CATIONS TO A'n'$M1_xM2_y(CN)_6$ CRYSTAL STRUCTURE
626
FORMING CATHODE WITH $A'_{n'}A_mM1_xM2_y(CN)_6$ PARTICLES

FIG. 7

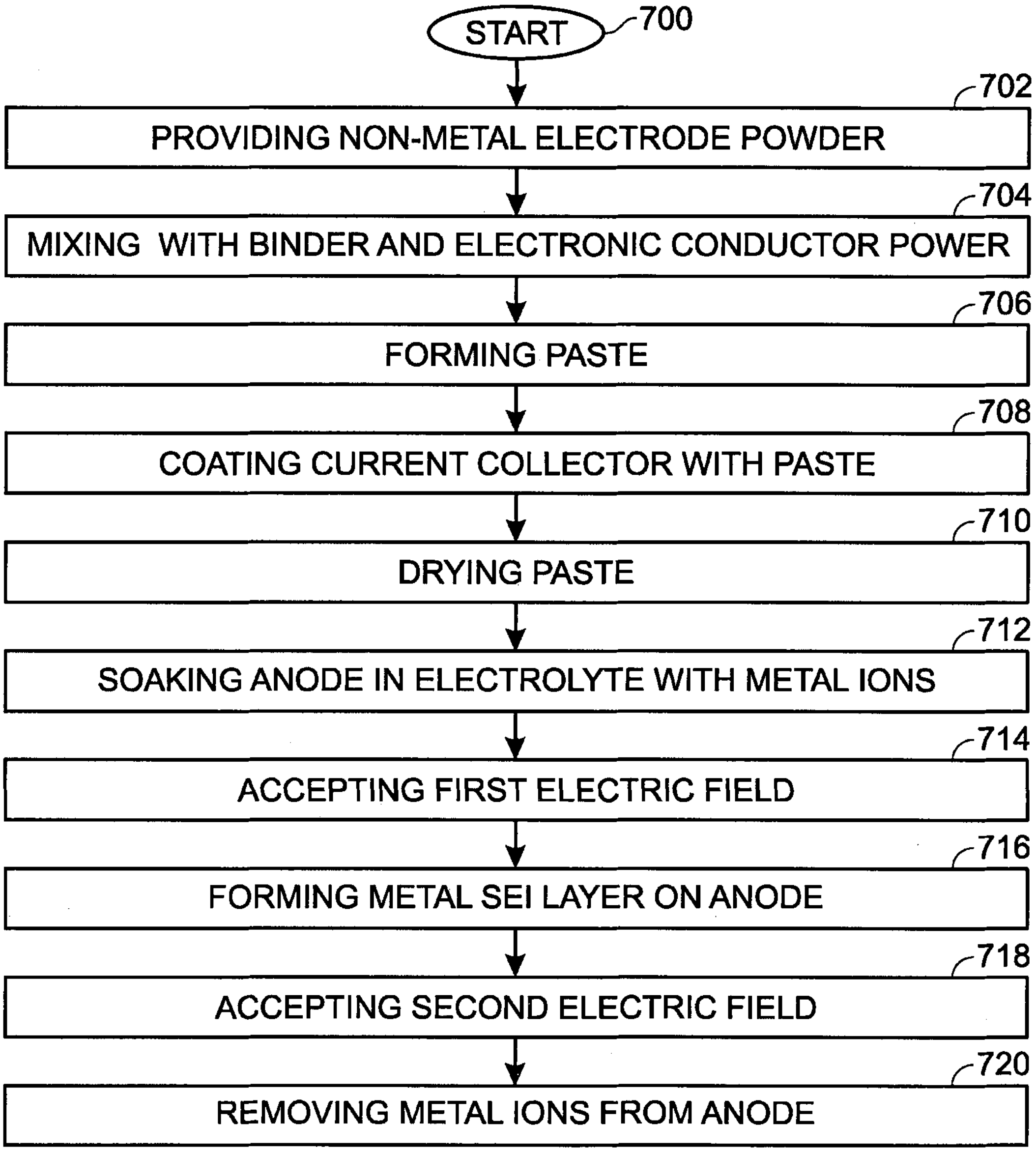

START
700
702
PROVIDING NON-METAL ELECTRODE POWDER
704
MIXING WITH BINDER AND ELECTRONIC CONDUCTOR POWER
706
FORMING PASTE
708
COATING CURRENT COLLECTOR WITH PASTE
710
DRYING PASTE
712
SOAKING ANODE IN ELECTROLYTE WITH METAL IONS
714
ACCEPTING FIRST ELECTRIC FIELD
716
FORMING METAL SEI LAYER ON ANODE
718
ACCEPTING SECOND ELECTRIC FIELD
720
REMOVING METAL IONS FROM ANODE

FIG. 8A

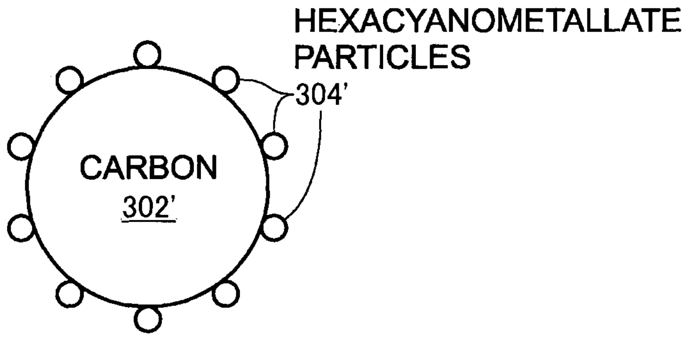


FIG. 8B

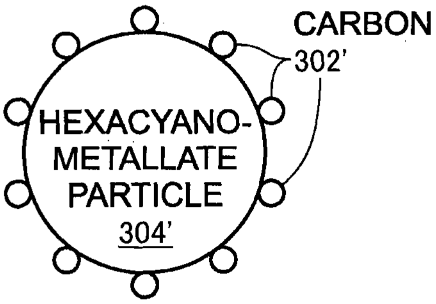


FIG. 9A

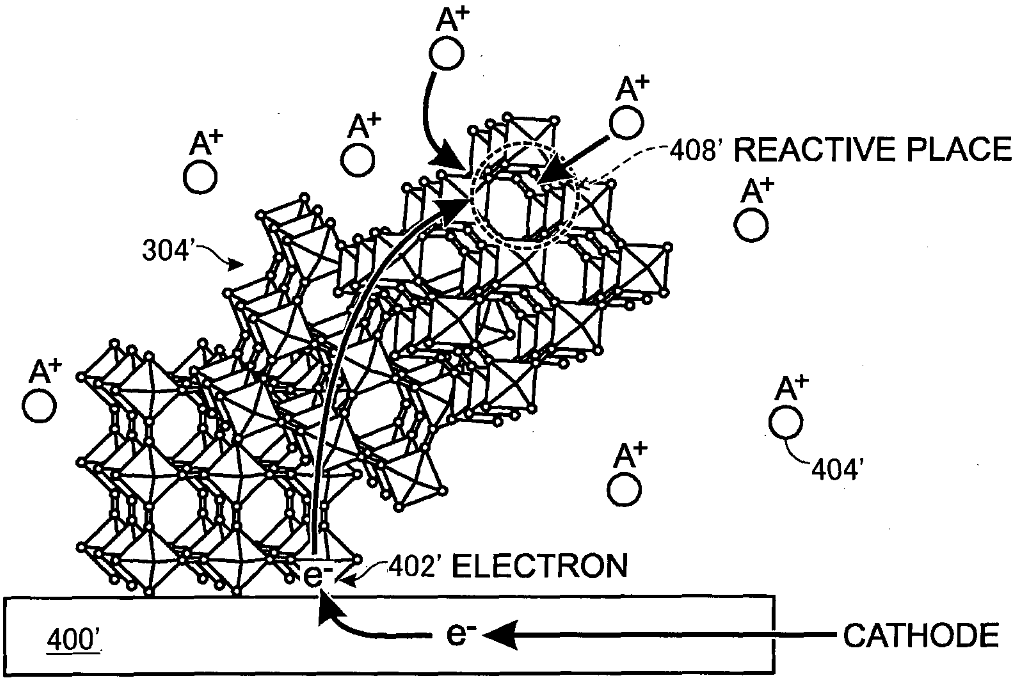


FIG. 9B

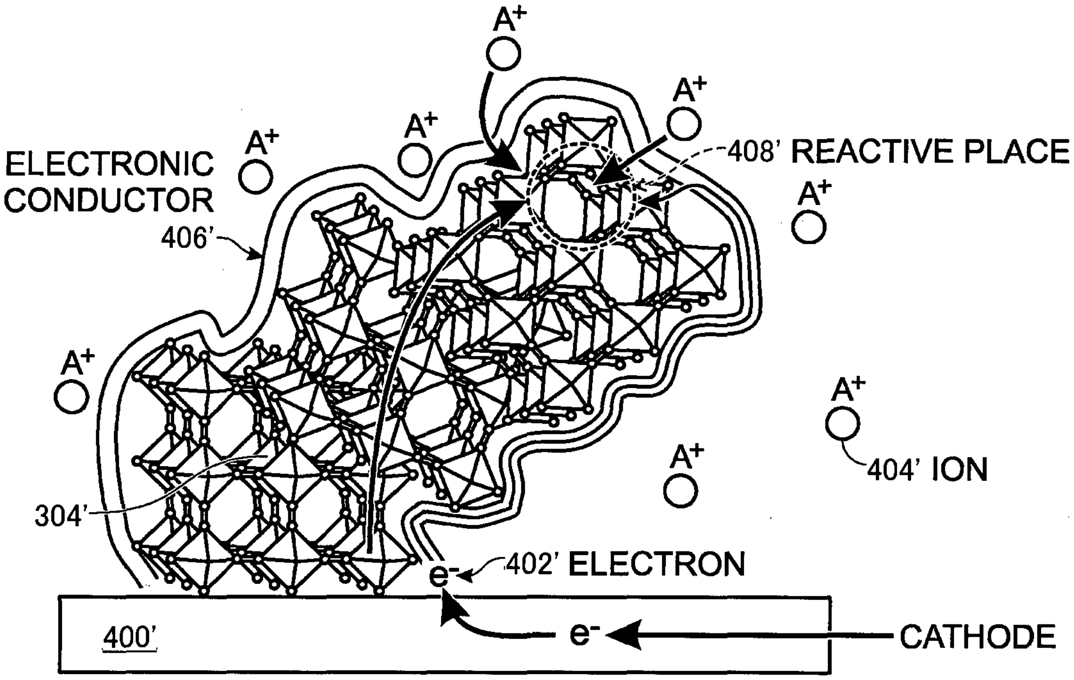

A+
ELECTRONIC CONDUCTOR
406'
408' REACTIVE PLACE
304'
404' ION
402' ELECTRON
e-
400'
CATHODE

FIG. 10

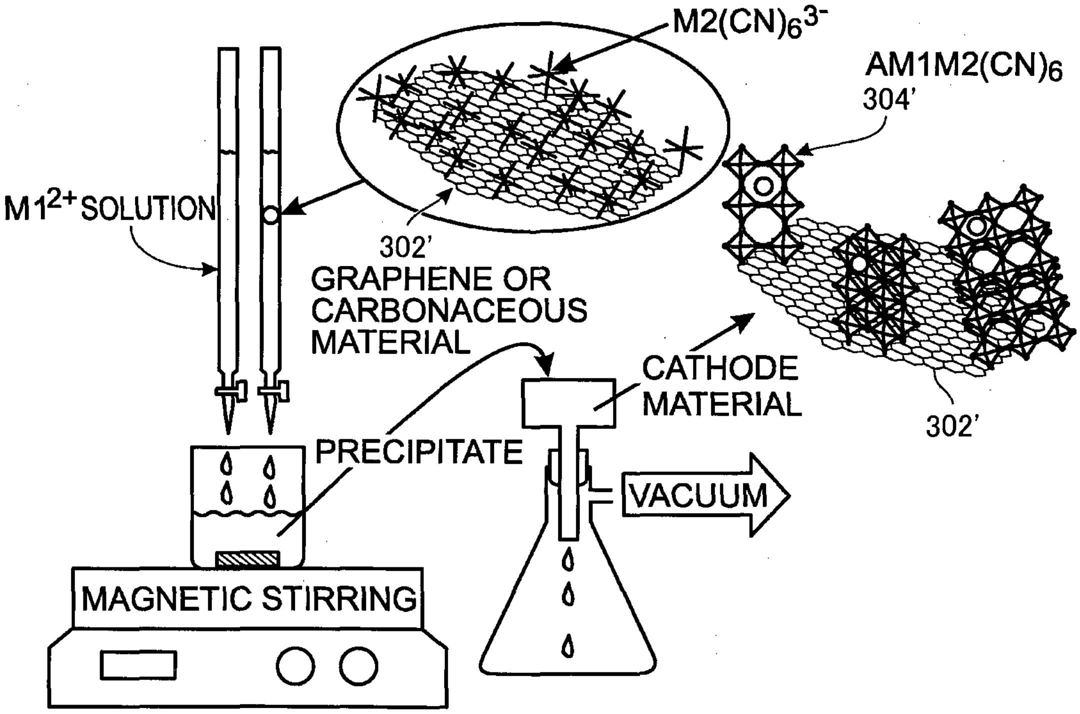

M2(CN)6 3-
AM1M2(CN)6
304'
M1 2+ SOLUTION
302'
GRAPHENE OR CARBONACEOUS MATERIAL
CATHODE MATERIAL
302'
PRECIPITATE
VACUUM
MAGNETIC STIRRING

FIG. 11

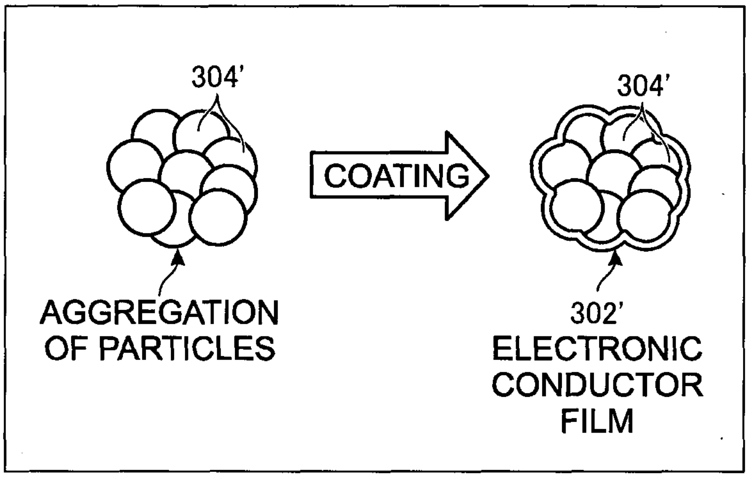

304'
COATING
304'
AGGREGATION OF PARTICLES
302'
ELECTRONIC CONDUCTOR FILM

FIG. 12

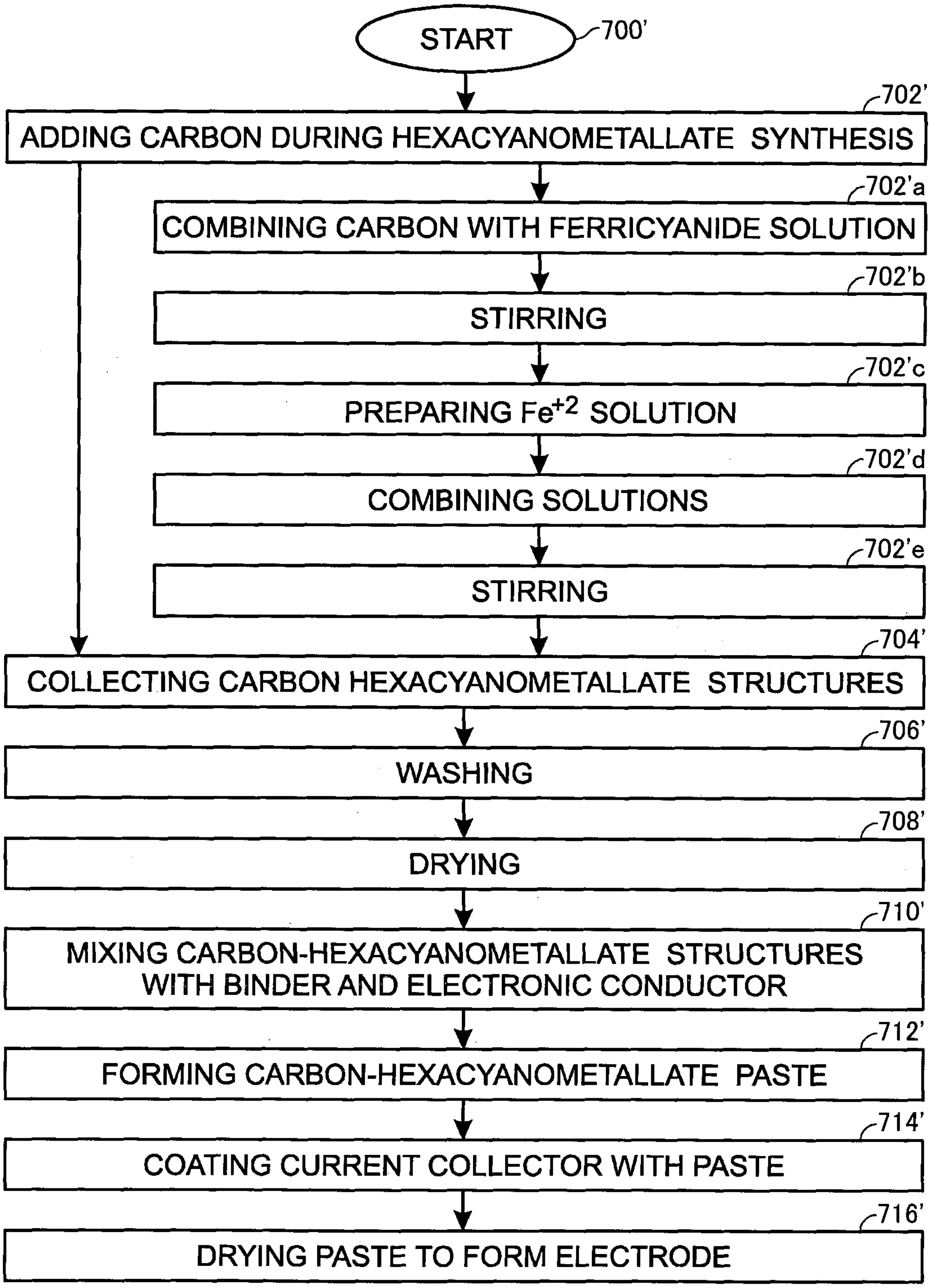

START
700'
702'
ADDING CARBON DURING HEXACYANOMETALLATE SYNTHESIS
702'a
COMBINING CARBON WITH FERRICYANIDE SOLUTION
702'b
STIRRING
702'c
PREPARING Fe+2 SOLUTION
702'd
COMBINING SOLUTIONS
702'e
STIRRING
704'
COLLECTING CARBON HEXACYANOMETALLATE STRUCTURES
706'
WASHING
708'
DRYING
710'
MIXING CARBON-HEXACYANOMETALLATE STRUCTURES WITH BINDER AND ELECTRONIC CONDUCTOR
712'
FORMING CARBON-HEXACYANOMETALLATE PASTE
714'
COATING CURRENT COLLECTOR WITH PASTE
716'
DRYING PASTE TO FORM ELECTRODE

FIG. 13

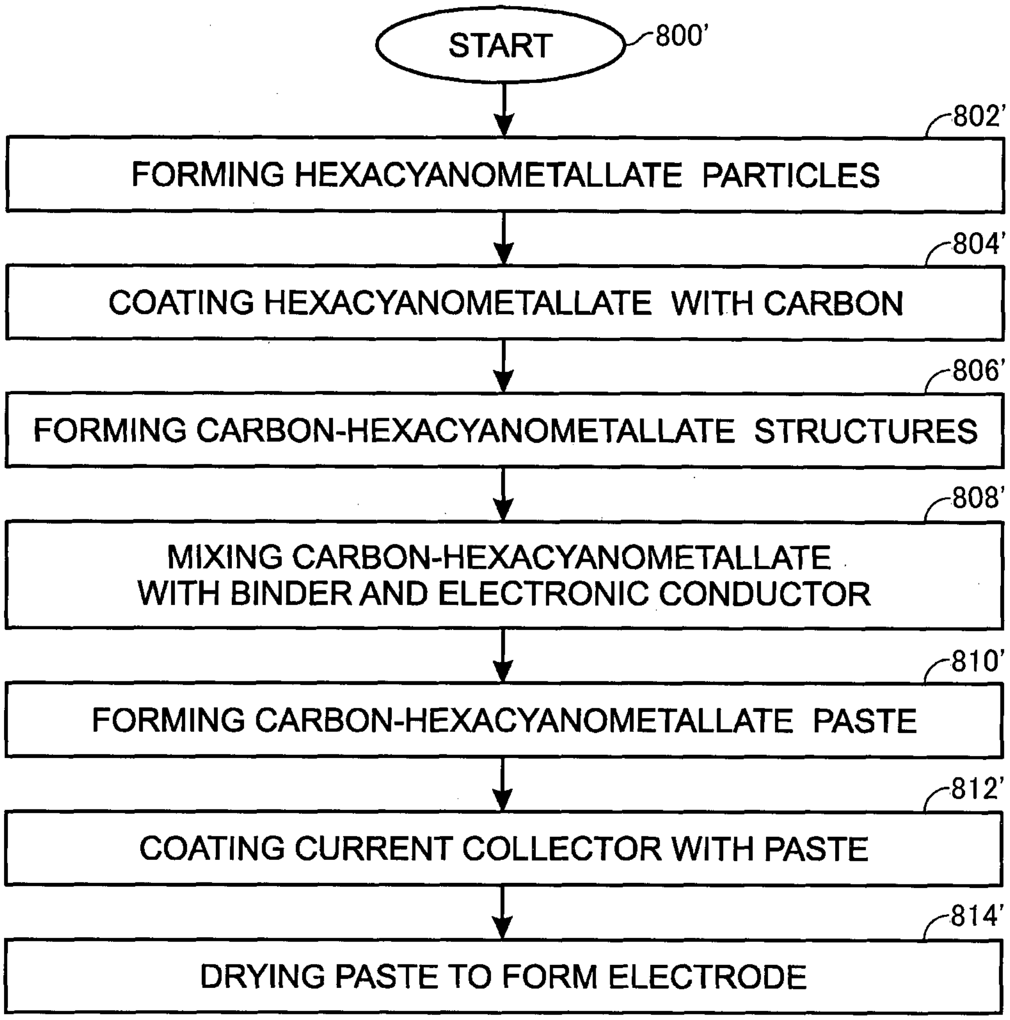

START
800'
802'
FORMING HEXACYANOMETALLATE PARTICLES
804'
COATING HEXACYANOMETALLATE WITH CARBON
806'
FORMING CARBON-HEXACYANOMETALLATE STRUCTURES
808'
MIXING CARBON-HEXACYANOMETALLATE WITH BINDER AND ELECTRONIC CONDUCTOR
810'
FORMING CARBON-HEXACYANOMETALLATE PASTE
812'
COATING CURRENT COLLECTOR WITH PASTE
814'
DRYING PASTE TO FORM ELECTRODE

FIG. 14

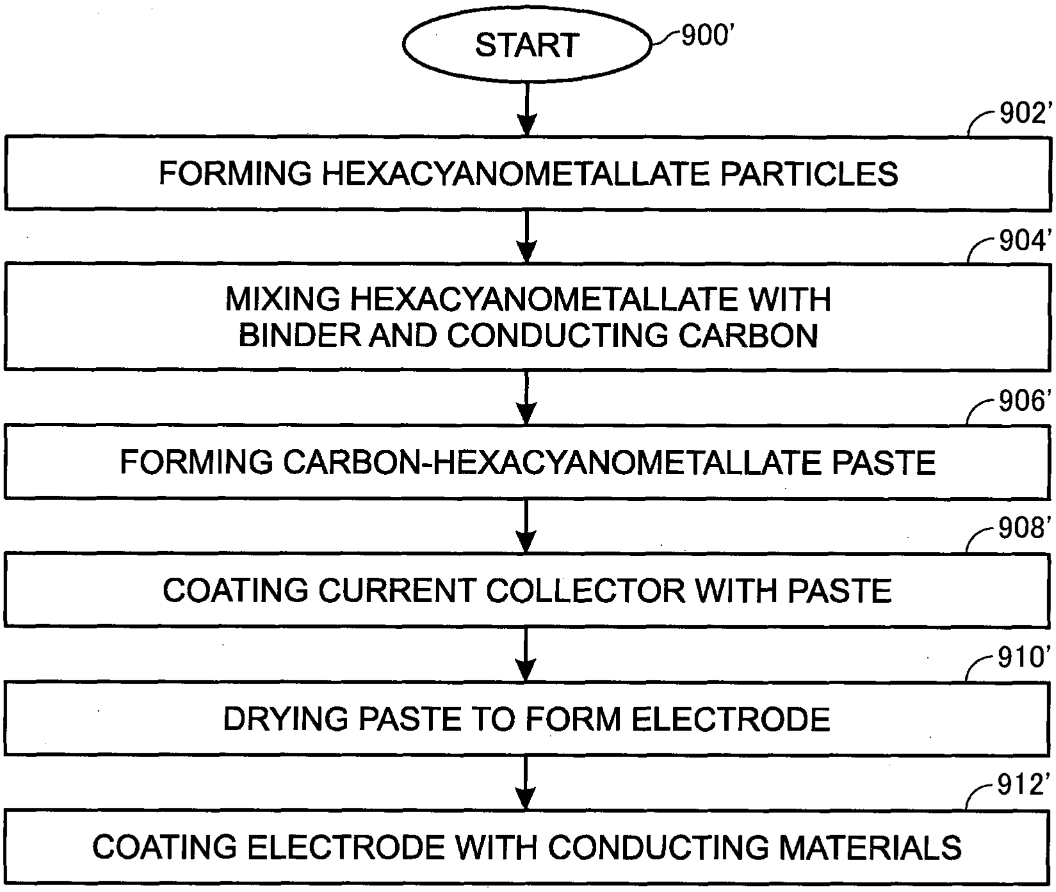

START
900'
902'
FORMING HEXACYANOMETALLATE PARTICLES
904'
MIXING HEXACYANOMETALLATE WITH BINDER AND CONDUCTING CARBON
906'
FORMING CARBON-HEXACYANOMETALLATE PASTE
908'
COATING CURRENT COLLECTOR WITH PASTE
910'
DRYING PASTE TO FORM ELECTRODE
912'
COATING ELECTRODE WITH CONDUCTING MATERIALS

FIG. 15A

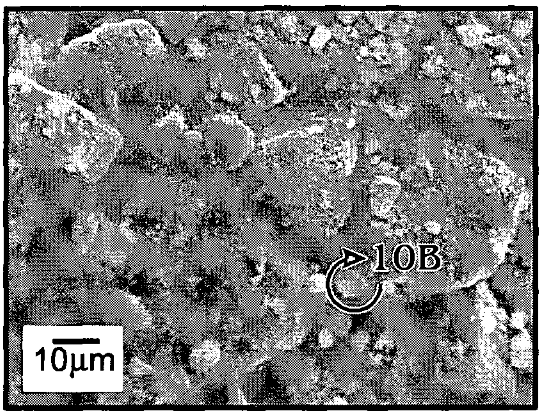


FIG. 15B

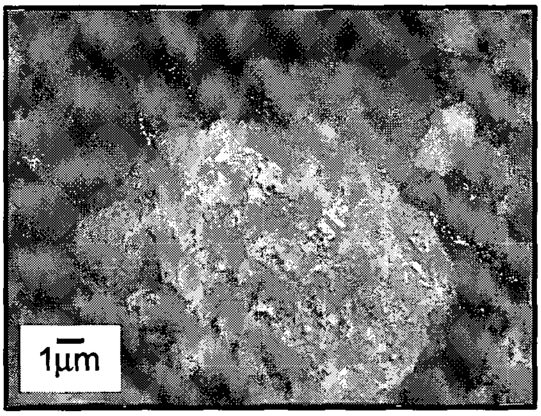


FIG. 16A

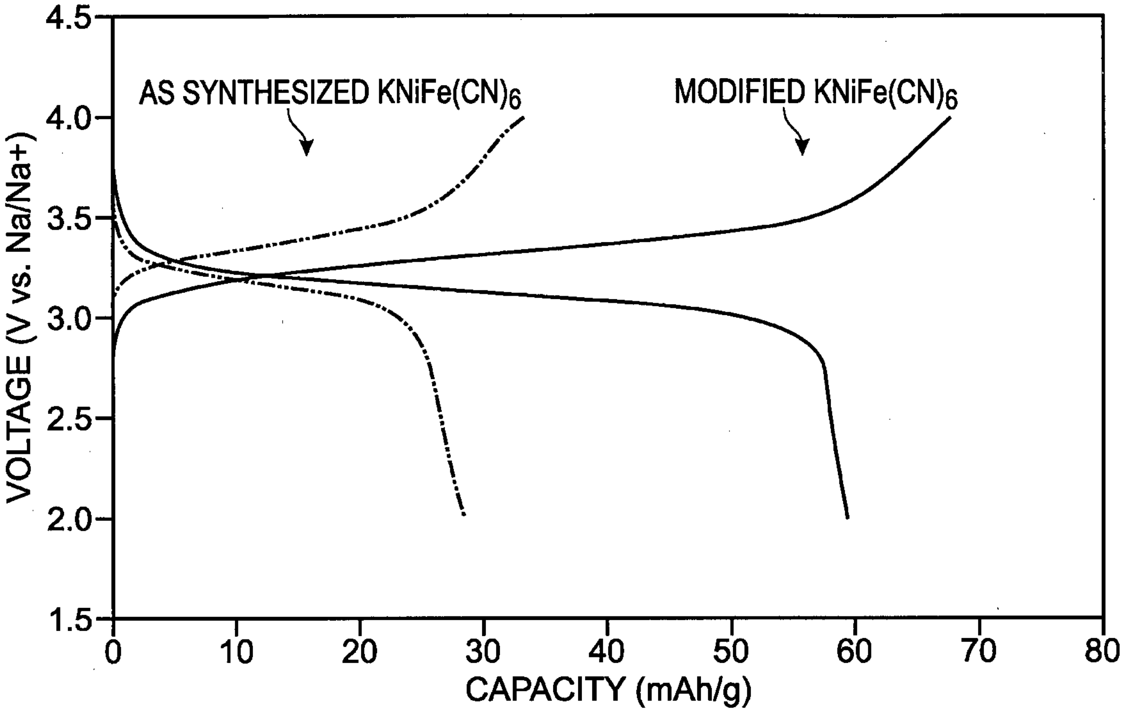
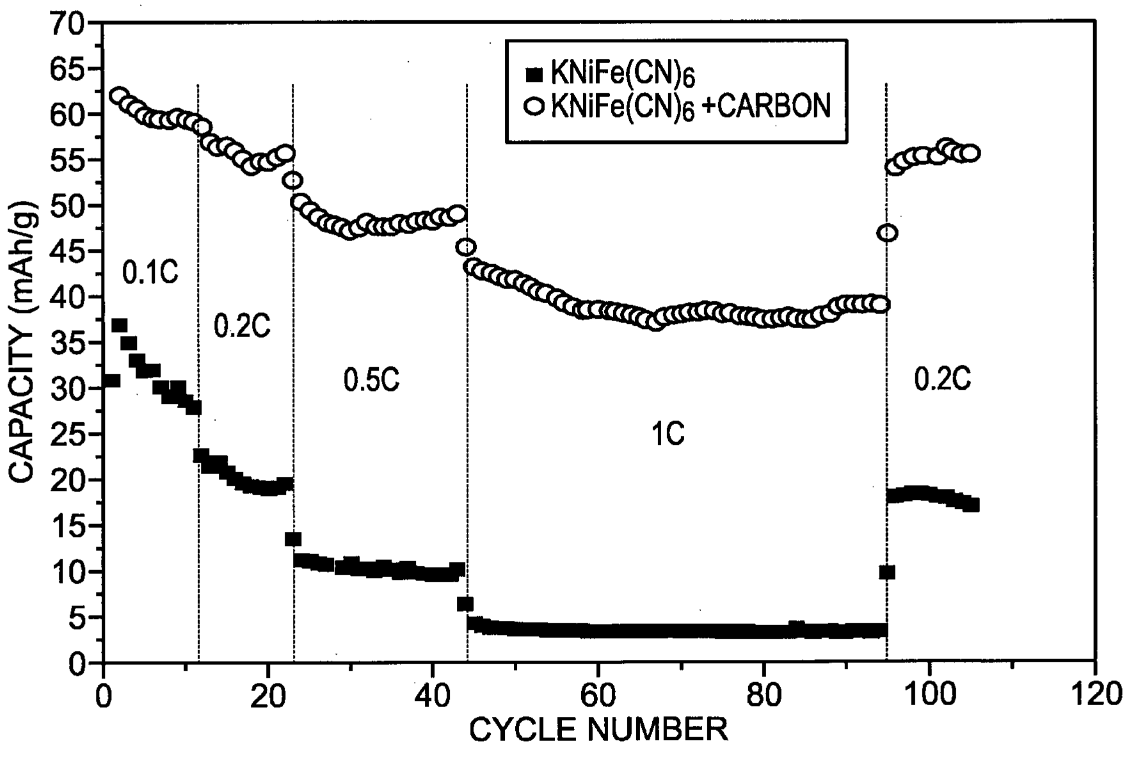


FIG. 16B



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2013/061961

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. See extra sheet

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl. H01M10/054, H01M4/139, H01M4/1397, H01M4/58, H01M10/052, H01M10/0525, H01M10/0565, H01M10/0566

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2013
Registered utility model specifications of Japan 1996-2013
Published registered utility model applications of Japan 1994-2013

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

JSTPlus(JDreamIII), JST7580(JDreamIII), JSTChina(JDreamIII)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y A	JP 10-21898 A (NIPPON GLASS FIBER CORPORATION) 1998.01.23, Claims 1,5 and 8, 【0013】【0023】【0024】【0026】-【0030】 FAMILY;NONE	1-6,11,12 6 7-10,13-44
Y	JP 2001-48527 A (TOYOTA MOTOR CORPORATION) 2001.02.20, 【0026】 FAMILY;NONE	6
A	Ali Eftekhari, Potassium secondary cell based on Prussian blue cathode, Journal of Power Sources, 2004.02.16, Vol.126/Issue1-2, pp.221-228	1-44
A	WO 2011/030790 A1 (NATIONAL INSTITUTE OF ADVANCED INDUSTRIAL SCIENCE AND TECHNOLOGY) 2011.03.17, ENTIRE TEXT FAMILY;NONE	1-44

☑ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
23.07.2013	06.08.2013

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2013/061961

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2012-46399 A (NATIONAL INSTITUTE OF ADVANCED INDUSTRIAL SCIENCE AND TECHNOLOGY) 2012.03.08, ENTIRE TEXT FAMILY;NONE	1-44
A	JP 5-27227 B2 (SEIKO INSTRUMENTS AND ELECTRONICS LTD) 1993.04.20, ENTIRE TEXT FAMILY;NONE	1-44
P,X	WO 2012/056765 A1 (NEC CORPORATION) 2012.05.03, Claims1,2 and 23, 【0035】【0068】【0070】-【0072】 FAMILY;NONE	45,46,48
A	JP 2002-246020 A (SONY CORPORATION) 2002.08.30, ENTIRE TEXT FAMILY;NONE	45-49

International application No.
PCT/JP2013/061961

CLASSIFICATION OF SUBJECT MATTER

H01M10/054(2010.01)i, H01M4/139(2010.01)i, H01M4/1397(2010.01)i, H01M4/58(2010.01)i, H01M10/052(2010.01)i, H01M10/0525(2010.01)i, H01M10/0565(2010.01)i, H01M10/0566(2010.01)i